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THE JOURNAL
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A Partition Function for Liquids from the Harmonic Oscillator Model

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(Received May 15, 1943)

The energy of the molecules of a liquid in their equilibrium positions and the frequency of vibration about those positions are expressed in terms of a parameter a, the average distance between the molecules. This follows from a formulation of an average potential or spherical symmetry from an assumed force field between pairs of molecules. The ordinary thermodynamic quantities are calculated from the resultant harmonic oscillator-partition function. Order-disorder effects are neglected.

INTRODUCTION

THE partition function Q for monatomic liquids and gases[2] may be defined as

$$Q=(2\pi mkT/h^2)^{3N/2}Q_\tau/N! \tag{1}$$

where

$$Q_\tau=\int\int\cdots\int_N \exp(-W/kT)d\tau_1 d\tau_2\cdots d\tau_N \tag{2}$$

is called the configuration integral.

W = potential energy of the whole system, referred to zero for infinite separation of the molecules and $d\tau_1$, $d\tau_2$ = elements of volume for molecule No. 1, No. 2, etc. In the harmonic oscillator or cell model the molecules are assumed to be confined to a small volume surrounding the equilibrium position; consequently, a configuration integral (per molecule) q_τ may be defined. Assuming spherical symmetry in the potential function,

$$q_\tau=4\pi\int_0^\infty \exp(-U/kT)r^2dr, \tag{3}$$

where U is the potential energy per molecule and r is the displacement of the molecule from its equilibrium position. If a is the average distance between molecules, the integral must converge at $a/2$, the radius of the cell, to have physical significance.*

In a real liquid the molecules may migrate from one part of the system to another, which has the effect of increasing the entropy by an amount R, the gas constant. To correct the cell model for this effect it is customary to relate the configuration integral per molecule to the configuration integral of the whole system as follows:

$$(eq_\tau)^N=Q_\tau/N!, \tag{4}$$

e^N being called the communal entropy factor.[3]

The potential energy U can be divided into two parts

$$U=U_0+U_r. \tag{5}$$

U_0 is the potential energy of the molecules in their equilibrium positions and U_r is the potential

[1] Research Assistant (1942–1943), University Research Institute.
[2] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, New York, 1940).

* The cell arrangement of the surrounding molecules would be destroyed if the central molecule passed into the adjoining cell.
[3] H. Eyring and J. Hirschfelder, J. Phys. Chem. **41**, 249 (1937).

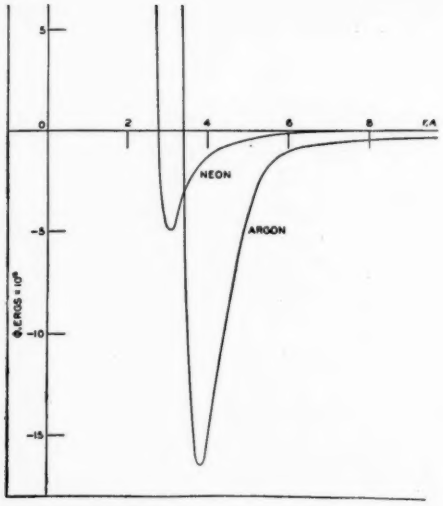

FIG. 1. Potential between pairs from Morse function, Eq. (16), with constants from Table I.

energy as a function of the displacement from those positions. For the harmonic oscillator model

$$U_r = Kr^2/2 \quad \text{or} \quad 2\pi^2\nu^2 m r^2, \tag{6}$$

where K is force constant and ν is the frequency defined by the equation

$$\nu = \frac{1}{2\pi}\left(\frac{K}{m}\right)^{\frac{1}{2}}. \tag{7}$$

On substituting U in Eq. (3)

$$q_r = 4\pi \exp(-U_0/kT)\int_0^\infty \exp\left(-\frac{Kr^2}{2kT}\right) r^2 dr \tag{8}$$

the partition function, Eq. (1), becomes

$$Q = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2} \times \exp(-NU_0/kT)\left(\frac{kT}{2\pi m\nu^2}\right)^{3N/2} e^N. \tag{9}$$

TABLE I.* Constants for Morse equation.

	Argon	Neon
	$u = 16.2\times10^{-8}$	35.5×10^{-10} erg A^6
	$v = 10.3\times10^{-11}$	83.2×10^{-13} erg A^{12}
R_1 in A	3.83	3.08
A in ergs	16.4×10^{-15}	4.87×10^{-15}
n in A^{-1}	1.66	2.06

* Values of u and v were taken from R. A. Buckingham, Proc. Roy. Soc. **A168**, 264 (1938).

By the usual methods this leads to the following thermodynamic functions:

$$A = NU_0 - 3NkT \ln(kT/h\nu) - NkT, \tag{10}$$

$$H = NU_0 - 3NkT + PV, \tag{11}$$

$$P = -N\delta U_0/\delta V - 3NkT\delta \ln \nu/\delta V. \tag{12}$$

To apply these formulae it is necessary to have U_0 and ν as functions of the volume.

FORMULATION OF THE CELL POTENTIAL

Lennard-Jones and Devonshire[4] have calculated the average potential energy of a molecule in its cell using as the potential between pairs of molecules,

$$\phi = u/R^{12} - v/R^6. \tag{13}$$

The constants u and v were determined from experimental data on the second virial coefficients of several gases.

The Morse function,[5]

$$\phi = A\exp[-m(R-R_1)] - B\exp[-n(R-R_1)], \tag{14}$$

formulated to express the potential energy of a diatomic molecule in terms of displacement R, from the position of minimum potential energy R_1, has the same general shape as Eq. (13). There are five constants in this form of the Morse function, but the condition that R_1 be the minimum requires

$$A/B = n/m. \tag{15}$$

These constants can be determined from the constants in the Lennard-Jones function by comparison of the intercepts R_0, the minimum points

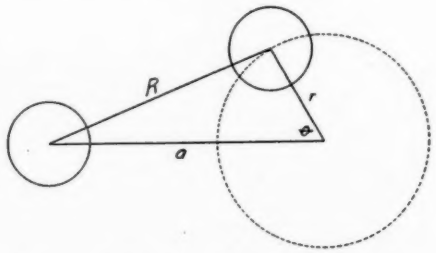

FIG. 2. Diagram indicating variables used in the averaging of the potential between pairs.

[4] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. **A163**, 53 (1937).
[5] P. M. Morse, Phys. Rev. **34**, 57 (1929).

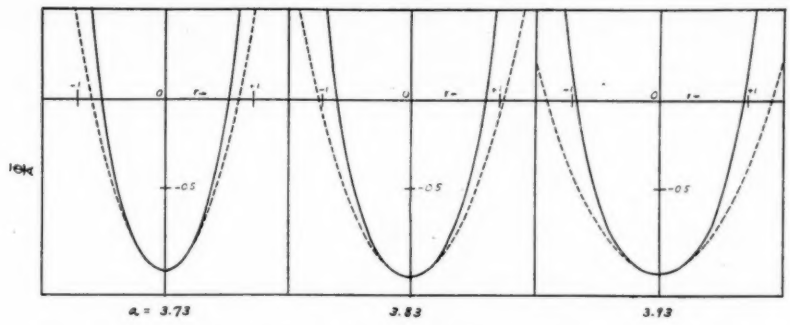

FIG. 3. The average potential of an argon molecule as a function of its displacement from the equilibrium position. The full line is from Eq. (26) and the dotted line from the expanded form in Eq. (27).

R_1, and the points of inflection R_2, of the two equations. Rather than make use of the point of inflection the ratio A/B will be set equal to $\frac{1}{2}$ as has been done by Morse. The Morse function then becomes

$$\phi = A\{\exp[-2n(R-R_1)] - 2\exp[-n(R-R_1)]\}. \quad (16)$$

It may be pointed out, however, that closer agreement of Eq. (14) with Eq. (13) may be obtained by the use of the point of inflection condition.

From Eq. (13),

$$R_0 = (u/v)^{1/6}, \text{ value of } R \text{ at the intercept}; \quad (17)$$

$$R_1 = (2u/v)^{1/6}, \text{ value of } R \text{ at the minimum}; \quad (18)$$

and

$$\phi(R_1) = -v^2/4u. \quad (19)$$

From Eq. (16)

$$n = \ln 2/(R_1 - R_0) \quad (20)$$

and

$$\phi(R_1) = -A. \quad (21)$$

Substituting (17) and (18) in (20)

$$n = 5.65/(u/v)^{1/6}. \quad (22)$$

Equating (19) and (21)

$$A = v^2/4u. \quad (23)$$

In Table I are given the values of A, n, and R_1 for argon and neon.

The potential curves for the Morse function are shown in Fig. 1.

Lennard-Jones and Devonshire averaged the potential energy of a molecule as it moves on the surface of a sphere, whose center is the equilibrium position of the molecule in its cell. The average potential energy due to one neighbor is calculated. See Fig. 2.

$$\bar{\phi} = (1/2)\int_0^{\pi} \phi(R)\sin\theta d\theta. \quad (24)$$

$\bar{\phi}$ is then multiplied by the number of nearest neighbors C ($C=12$ for a face-centered cubic structure), and divided by two to obtain the potential energy per molecule, U.

$$U = C\bar{\phi}/2. \quad (25)$$

Substitution of the Morse function into (24) and (25) gives

$$U = \frac{CA}{2n^2a}\left\{\frac{\exp[-2n(a-R_1)]}{4}\cdot\left[\left(\frac{2na+1}{r}\right)\sinh 2nr - 2n\cosh 2nr\right] - 2\exp[-n(a-R_1)]\left[\left(\frac{na+1}{r}\right)\sinh nr - n\cosh nr\right]\right\}, \quad (26)$$

where a is the average distance between molecules and r is the displacement of the molecule from its equilibrium position. In Fig. 3 are shown plots (in full line) of $\bar{\phi}/A = 2U/CA$ from Eq. (26) for several values of a.

Expanding (26) in powers of r and dropping

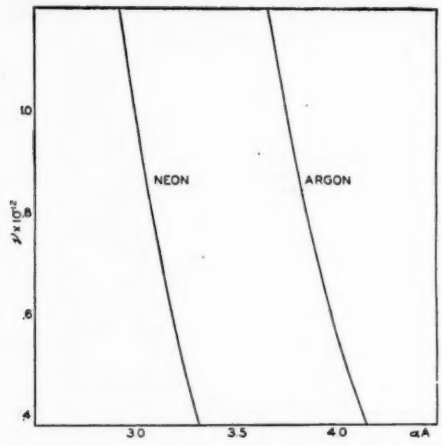

FIG. 4. Average vibration frequency as a function of the average distance between molecules, calculated from Eqs. (29) and (7).

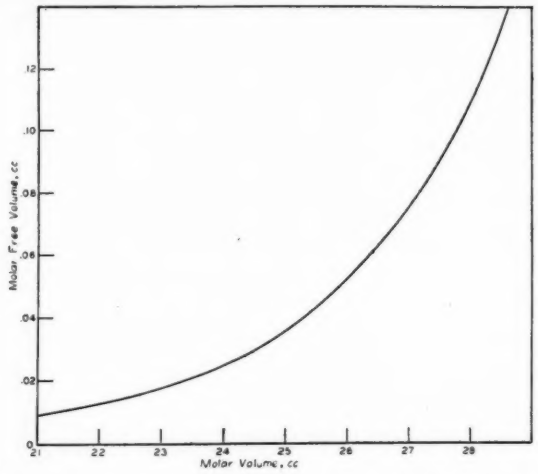

FIG. 5. Free volume of argon as a function of the molar volume from Eq. (32).

terms containing fourth and higher powers in r,

$$U=\frac{CA}{2}\{\exp[-2n(a-R_1)]-2\exp[-n(a-R_1)]\}+\frac{CA}{6a}\{2\exp[-2n(a-R_1)](n^2a-n)-\exp[-n(a-R_1)](n^2a-2n)\}r^2. \quad (27)$$

This expanded form is shown (in dotted line) in Fig. 3. Rice[6] has obtained an average potential by calculating the effect of a given displacement on each of the nearest neighbors.

Comparison of (27) with (5) and (6) sets

$$U_0=\frac{CA}{2}\{\exp[-2n(a-R_1)]-2\exp[-n(a-R_1)]\} \quad (28)$$

and

$$K=\frac{CA}{3a}\{2\exp[-2n(a-R_1)](n^2a-n)-\exp[-n(a-R_1)](n^2a-2n)\}, \quad (29)$$

K is now expressed in terms of a, and the average frequencies may be calculated by Eq. (7). In Fig. 4 the average frequencies are plotted against a. Maximum frequencies calculated from the Debye temperatures given by Clusius[7] are 1.7×10^{12} for argon and 1.3×10^{12} for neon. Kane[8] has also computed frequencies as functions of intermolecular distances, the treatment involving the heat of sublimation and the elastic constants of the crystal.

PARTITION FUNCTION

If U from Eq. (27) is substituted into (3), (4), and (9) the following partition function results.

$$Q=\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\exp\left\{-\frac{NCA}{2kT}[\exp\{-2n(a-R_1)\}-2\exp\{-n(a-R_1)\}]\right\}\times\left(\frac{6\pi kTa}{CA\{2\exp[-2n(a-R_1)](n^2a-n)-\exp[-n(a-R_1)](n^2a-2n)\}}\right)^{3N/2}e^N. \quad (30)$$

The effect on the configuration integral of dropping fourth and higher power terms in r was checked by graphical integration of the expanded form, Eq. (27), and the unexpanded form, Eq. (26). As could be predicted from an inspection of Fig. 3 the deviation of the two integrals becomes greater, the larger the values of a. In general the approximation is not valid for a greater than R_1.

[6] O. K. Rice, J. Am. Chem. Soc. **63**, 3 (1941).

[7] K. Clusius, Zeits. f. physik. Chemie **B31**, 459 (1936); K Clusius and L. Riccoboni, Zeits. f. physik. Chemie **B38**, 81 (1937).

[8] G. Kane, J. Chem. Phys. **7**, 603 (1939).

However, it is doubtful whether the cell model has any significance for large values of a; consequently, the approximation does not limit seriously the legitimate use of the model.*

FREE VOLUME

The partition function may be set up using "the smoothed potential" model,[9] according to which the molecule may move in a uniform potential field in a small volume element known as the free volume, v_f;

$$Q=\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\exp\left(-NU_0/KT\right)(v_f)^N e^N. \quad (31)$$

On comparison with Eq. (30)

$$v_f=\left(\frac{6\pi kTa}{CA\{2\exp\left[-2n(a-R_1)\right](n^2a-n)-\exp\left[-n(a-R_1)\right](n^2a-2n)\}}\right)^{\frac{1}{3}}. \quad (32)$$

In Fig. 5 the molar free volume, Nv_f, is plotted against the molar volume of argon at 80° Abs. Eyring[3,10] and his co-workers have developed the concept of free volume extensively, formulating it in terms of measurable quantities. Eyring estimates the molar free volume of argon at the melting point from the entropy of liquid argon to be 0.15 cc. Using specific heats he estimates a value of 0.35.

EQUATION OF STATE

The equation of state can be obtained by substituting in (12). It is more convenient, however, to use the formula

$$P=kT\frac{\delta\ln Q}{\delta V}=kT\frac{\delta\ln Q}{\delta a}\frac{\delta a}{\delta V} \quad (33)$$

obtaining, since $a^3=\gamma V$ and $\gamma=\sqrt{2}$ for a face-centered structure,

$$P=\frac{kT\gamma}{3a^2}\left\{\frac{CAn}{KT}(\exp\left[-2n(a-R_1)\right]-\exp\left[-n(a-R_1)\right])+\frac{3}{2}\left(\frac{1}{a}-\frac{\exp\left[-n(a-R_1)\right](6n-4n^2a)-(3n-n^2a)}{\exp\left[-n(a-R_1)\right](2na-2)-(na-2)}\right)\right\}. \quad (34)$$

PVT curves for argon are given in Fig. 6. At the higher temperatures these curves have minima. Kane[8] has discussed such minima in terms of the melting point of the solid. Simon and Kippert[11] have obtained $(\delta P/\delta T)_V$ values for argon of 38.6 atmospheres per degree at 76 degrees and 25.0 at 86 degrees absolute. Equation (34) gives a value of 30 atmospheres per degree at low molar volumes and 35 atmospheres per degree at higher molar volumes, independent of temperature.

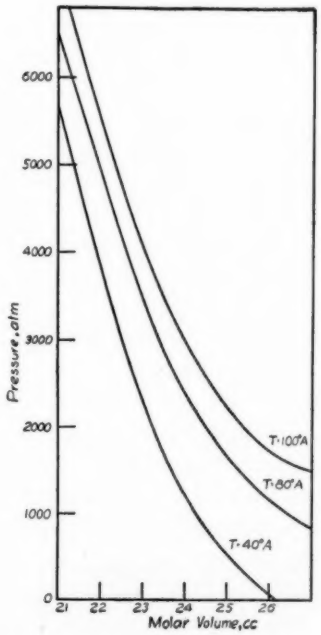

FIG. 6. PVT curves for argon, from Eq. (34).

HEAT OF VAPORIZATION

The heat content of a monatomic liquid was formulated in Eq. (11). If this is subtracted from

* The theory should hold only for liquids at lower temperatures and higher pressures. The partition function may also be used for the solid state in which case the factor e^N would be omitted.

[9] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Macmillan, New York, 1939).

[10] J. O. Hirschfelder, D. P. Stevenson, and H. Eyring, J. Chem. Phys. **5**, 896 (1937); J. F. Kincaid and H. Eyring, J. Chem. Phys. **6**, 620 (1938).

[11] F. Simon and F. Kippert, Zeits. f. physik. Chemie **135**, 113 (1928).

the heat content of the gas one obtains the heat of vaporization.

$$\Delta H = H_{\text{gas}} - H_{\text{liq}} = 5/2(NkT) - NU_0 - 3NkT = -NU_0 - \tfrac{1}{2}NkT. \quad (35)$$

The PV term in H_{liq} may be neglected at ordinary pressures. For argon at 80 degrees absolute the heat of vaporization from Eq. (35) is 1350 calories per mole and for neon at twenty-six degrees 400 calories per mole, at $a = R_0$, to be compared with the experimental values[12] of 1500 and 405 calories per mole, respectively.

We wish to express our appreciation to Professors W. A. Felsing and H. Eyring for their interest in the progress of the work.

[12] W. M. Latimer and J. H. Hildebrand, *Reference Book of Inorganic Chemistry* (Macmillan Company, New York, 1940).

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Specific Heats of Carbon Tetrafluoride from Supersonic Measurements

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(Received May 10, 1943)

Measurements of the velocity and absorption of supersonic waves in carbon tetrafluoride were made over a range of pressures for each of two different frequencies. From the dispersion and absorption curves so obtained, the specific heat for equilibrium conditions, that portion of the specific heat due to intra-molecular vibrations, and the mean lifetime of a quantum of vibrational energy were calculated.

INTRODUCTION

THE velocity and absorption of supersonic waves in carbon tetrafluoride have been measured over an effective frequency range from 105.2 kc to 2,195 kc, which represents the major portion of a dispersion region. The measurements were actually made at two frequencies, 290.7 kc and 615.6 kc, while the pressure of the gas was varied from $\frac{1}{3}$ to 3 atmospheres. The effective frequency at atmospheric pressure is then given by the ratio of frequency to pressure. The temperature of the various measurements ranged from 20.5°C to 23.5°C, but during any one measurement it never varied more than 0.1° and was known to the same degree of precision.

A very pure sample of carbon tetrafluoride was furnished by Dr. J. H. Simons, the director of the fluorine research laboratories of The Pennsylvania State College. The supersonic chamber in which the measurements were made had a leak rate, when thoroughly degassed and evacuated, of 1 micron per hour or less. The glass storage bulb in which the gas was confined between runs had a much lower leak rate—a few microns per day. The original gas was stated to contain certainly less than one percent and probably less than one-tenth percent of impurities. The above stated leak rates over the total period of the experiments would introduce less than one one-hundredth of one percent of impurities. These statements on purity were verified by a calculation of the molecular weight of the gas remaining at the close of the period of measurements. The calculations, based on density measurements, gave a value of 88.2 ± 0.2; which is to be compared to the theoretical value of 88.01.

EXPERIMENTAL

The measurements were made with the Pierce interferometer described by Telfair and Pielemeier.[1] The absorption per wave-length was calculated from the logarithmic decrement of the plate current variation. This method has received ample experimental[2,3] and theoretical[4] verifi-

[1] D. Telfair and W. H. Pielemeier, Rev. Sci. Inst. **13**, 122 (1942).
[2] W. H. Pielemeier, Phys. Rev. **34**, 1184 (1929).
[3] A. van Itterbeek and P. Mariens, Physica **4**, 207 (1937).
[4] H. C. Hardy, Doctorate Dissertation, The Pennsylvania State College (1941).

cation. Absorption and dispersion curves were obtained by plotting the measured values against the common logarithm of the ratio of frequency in cycles per second to pressure in atmospheres. The results, corrected to 22°C, are given in Table I and are shown in Fig. 1.

It will be seen that the absorption values for runs Nos. 4, 5, and 6 are not in agreement with the other values which yield a smooth symmetrical curve. No explanation of this discrepancy can be given unless it be that an inhomogeneity of the sound field existed which, together with that part of the absorption due to the inhomogeneity of the field,[5] was a function of pressure.

To obtain values for use in calculations it was necessary to extrapolate the velocity and the velocity squared curves at each end until they became flat. These extrapolations, shown by the broken lines in the figure, give the following values:

$$V_0=178.2\pm0.4 \text{ meters/sec.},$$
$$V_0^2=31{,}800\pm100 \text{ (meters/sec.)}^2,$$
$$V_\infty=192.2\pm0.3 \text{ meters/sec.},$$
$$V_\infty^2=36{,}950\pm100 \text{ (meters/sec.)}^2,$$

where V_0 is the velocity corresponding to very low frequencies and V_∞ is the velocity corresponding to very high frequencies. As an indication of the smallness of the error in the extrapolation, the agreement between the velocity and the velocity squared values so obtained may be noted.

TABLE I.

Run No.	log f/p	$\mu_{22°}$	$V_{22°}^2$ (meters/sec.)^2	$V_{22°}$ (meters/sec.)
7	5.022	0.202	32,060±10	179.08±0.04
1	5.172	0.276	32,460±30	180.2 ±0.1
2	5.312	0.353	32,850±50	181.3 ±0.1
3	5.462	0.415	33,450±70	182.9 ±0.2
4	5.596	0.458	34,000±70	184.4 ±0.2
5	5.765	0.462	34,960±200	186.7 ±0.5
6	6.007	0.434		
12	5.329	0.360	32,710±70	180.9 ±0.2
13	5.505	0.429	33,550±200	183.2 ±0.6
11	5.802	0.440	35,190±40	187.6 ±0.1
10	6.002	0.389	36,000±40	189.7 ±0.1
9	6.209	0.290	36,630±40	191.4 ±0.1
8	6.341	0.224	36,820±40	191.9 ±0.1

In runs Nos. 1–7, f=290.7 kc.
In runs Nos. 8–13, f=615.6 kc.

[5] E. J. Pumper, J. Phys. U.S.S.R. **1**, 411 (1939). Pumper considers the case with no internal absorption, and obtains at constant frequency the expression for the absorption to be $\mu=\mu_0+\mu_e$, where μ_0 is a constant depending on the inhomogeneity of the sound field and μ_e is directly proportional to $1/p$. Classical formulation further shows μ_e to be proportional to f/p.

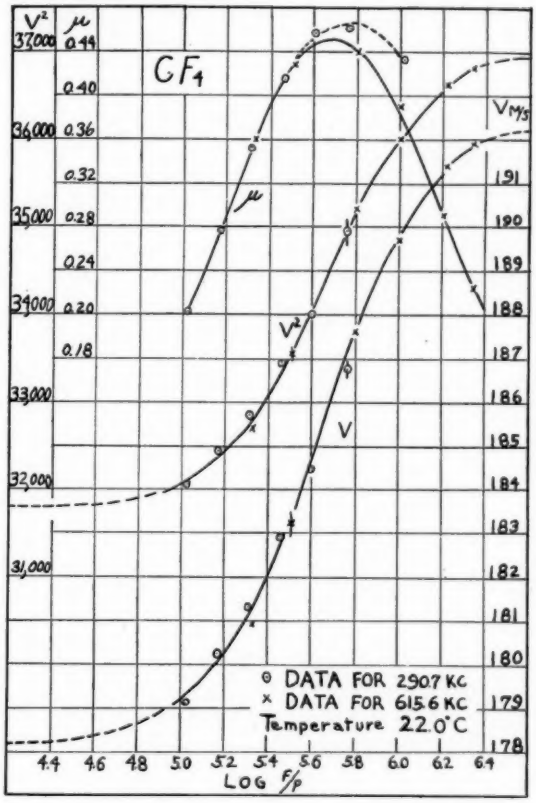

FIG. 1.

The value of $(f/p)_m$, for maximum absorption, is 480±10 kc/atmos.; and the location of the inflection point of the velocity squared curve, $(f/p)_w$, is 470±10 kc/atmos. (The subscript "w" is used, following some of the literature, for "Wendepunkt.") This latter value was obtained from the coordinates of V_w^2, where V_w^2 is given by

$$V_w^2=(V_0^2+V_\infty^2)/2.$$

The maximum absorption, obtained from the solid curve, is 0.45±0.1 per wave-length.

CALCULATIONS

To obtain the specific heats from the velocities use was made of the equation

$$V^2=RT/Mg(1+Rd/C),$$

where

$$g=1+2bp/RT-2ap/R^2T^2,$$
$$d=1+ap/R^2T^2,$$

and "a" and "b" are the van der Waals correction terms. Since no equation of state data is available for carbon tetrafluoride an attempt was made to estimate values for "a" and "b." A comparison was made among the values of "a" and "b," the critical pressure and temperature, and the melting and boiling points of CH_4, CCl_4, SiH_4, SiF_4, and SnF_4. The results, which are correct only as to order of magnitude, are: $a=0.0065$ and $b=0.0022$.

The use of these values and the values of V_0 and V_∞ in the above equation yields for 22.0°C:

$$C_0=13.5\pm0.5 \text{ cal./mole},$$
$$C_\infty=6.0\pm0.2 \text{ cal./mole},$$

where C_0 is the equilibrium value of the specific heat at constant volume and C_∞ is the effective value at infinitely high frequencies. The internal specific heat, caused by intramolecular vibrations, is given by the difference between the above two specific heats.

$$C_i=C_0-C_\infty=7.5\pm0.7 \text{ cal./mole}.$$

The value stated above for C_∞ agrees well with $C_\infty^\infty=3R$ at infinitely low pressures.

As a check on these values the absorption per wave-length may be calculated.

$$\mu=\pi RC_i/[C_0(C_0+R)C_\infty(C_\infty+R)]^{\frac{1}{2}}$$
$$=0.47\pm0.06.$$

The observed value, taken from the curve, is 0.45 ± 0.1.

The above value of C_0 at atmospheric pressure is considerably larger than the value of 11.9 predicted by Eucken and Bertram[6] for C_0 at infinitely low pressures. The cause of this discrepancy is undoubtedly the values of the frequencies of vibrations which they used; they were not at all in agreement with later values given by Yost[7] and Bailey.[8]

From the smoothness of the curves and values of C_∞ and C_i, it is apparent that carbon tetrafluoride has but one relaxation time. The mean value of the relaxation time at one atmosphere has been calculated from both the absorption and the dispersion curve by means of the equations

$$\beta=\frac{1}{2\pi(f/p)_m}\left[\frac{(C_0+R)C_0}{(C_\infty+R)C_\infty}\right]^{\frac{1}{2}}$$

and

$$\beta=\frac{1}{2\pi(f/p)_w}\frac{C_0}{C_\infty}.$$

The values so obtained are

β (by absorption curve) $=(7.4\pm0.5)\times10^{-7}$ sec.,

β (by dispersion curve) $=(7.8\pm0.5)\times10^{-7}$ sec.,

giving a mean value of

$$\beta=(7.6\pm0.5)\times10^{-7} \text{ sec.}$$

[6] A. Eucken and A. Bertram, Zeits. f. physik. Chemie **B31**, 361 (1936).
[7] D. M. Yost, J. Chem. Phys. **4**, 325 (1936).
[8] C. R. Bailey, J. Chem. Phys. **5**, 274 (1937).

The Structure of Liquid Carbon Tetrachloride

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Monochromatic x-ray diffraction patterns of liquid CCl_4 at 25°C and at −20°C have been analyzed to obtain radial electron density distribution curves. These curves show discrete peaks corresponding to distances between atoms in a molecule (1.7A and 2.9A at −20°C; 1.74A and 2.92A at 25°C), as well as other peaks (3.6A, 4.1A, and 6.4A at −20°C; 4.0A and 6.3A at 25°C) which are not discrete and which represent distances between atoms in different molecules.

INTRODUCTION

APPLICATION of the generalized Fourier method[1] to x-ray diffraction patterns of polyatomic substances has been made for a wide variety of glasses[2] and for a few liquids.[3] In a recent article,[4] this type of analysis has been applied to the diffraction pattern of carbon tetrachloride, giving as a result, the radial electron distribution curve for this substance. Previous to the appearance of this article on liquid carbon tetrachloride, the present writers had carried out an extensive series of experiments on the same liquid at two temperatures. In addition to presenting, herewith, the effect of temperature on the distribution curve, certain aspects of these curves are compared with those of the recently reported distribution curve for the same liquid.

EXPERIMENTAL

Most of the diffraction patterns were taken with Mo $K\alpha$ radiation and photographic film, but one excellent pattern was obtained with Ag $K\alpha$ radiation and a Geiger counter as detector of the scattered radiation. In the photographic method, a large camera of 9.20-cm radius was used to insure sufficiently accurate determinations of scattering angles. A total of twelve useful patterns were obtained in this manner at 25°C, as well as two fairly good patterns at −20°C. Six prominences appeared on all films, and on six films, a weak seventh peak was measurable. Eight of the 25°C films showed no clearly defined seventh peak, presumably because of under-exposure. The pattern obtained with the Geiger counter and Ag $K\alpha$ radiation gave a clear indication and satisfactory measure of the seventh peak.

Several types of sample were tried. A free-stream sample was first used and later discarded when it had been shown that patterns so obtained were indistinguishable from those using a thin-walled glass capillary. Because of possible question of the absorption correction applied to cylindrical samples which are not uniformly and completely bathed in incident radiation, several of the above patterns were taken with a flat sample contained between thin Cellophane walls. Tests for chemical impurity introduced into the CCl_4 by the use of Cellophane gave no indication of contamination. The cylindrical samples were 1.4 mm and 1.6 mm in diameter and the flat sample was 0.55 mm thick. As used in all cases of flat sample exposures, the normal to the sample face made an angle of 45° with the incident beam in order to enhance the weak seventh peak.

Appropriate corrections and preparations for curve-fitting were made in the usual manner,[1] and the final curves for the two temperatures are shown in Figs. 1 and 2. From these curves, the $si(s)$ function was determined and subjected to an analysis to determine the radial electron density distribution as shown in Fig. 3 for the two temperatures.

DISCUSSION OF RESULTS

Perhaps the most important departure between the present distribution curves and the one shown by Eisenstein[4] is in the appearance in the present work of discrete peaks for the C–Cl and the Cl–Cl distances within a molecule. In a

[1] B. E. Warren, H. Krutter, and O. Morningstar, J. Am. Ceram. Soc. **19**, 202 (1936).
[2] E.g., J. Biscoe, A. G. Pincus, C. S. Smith, and B. E. Warren, J. Am. Ceram. Soc. **24**, 116 (1941).
[3] E.g., G. G. Harvey, J. Chem. Phys. **7**, 878 (1939).
[4] A. Einstein, Phys. Rev. **63**, 304 (1943).

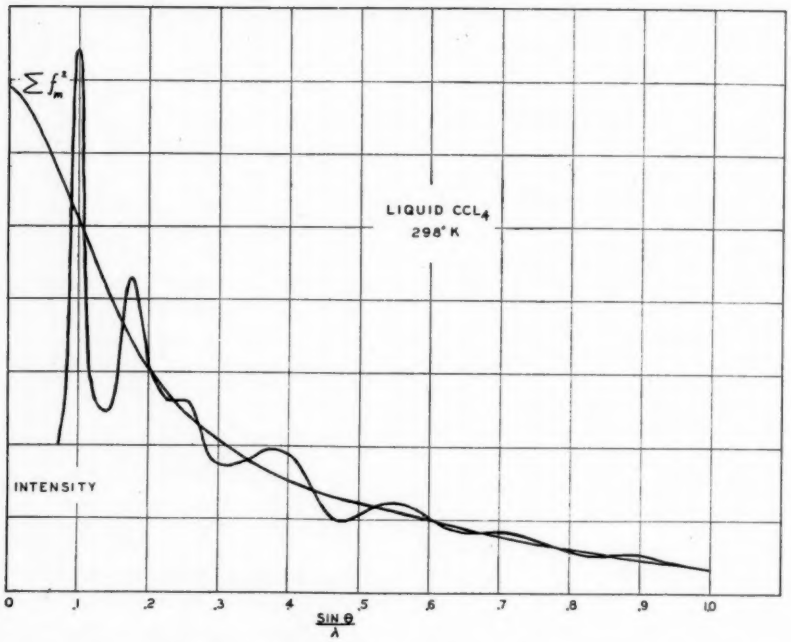

FIG. 1. Intensity pattern for liquid CCl_4 at 298°K, fully corrected and fitted to the independent coherent curve.

critical review of work on x-ray and electron diffraction by gaseous CCl_4, Brockway[5] concludes that the most probable value of the C–Cl distance in molecules of gaseous CCl_4 is 1.75A, from which the Cl–Cl distance should be 2.87A. In the present work, the C–Cl distance is found to be about 1.74A for 25°C and 1.7A for −20°C; the Cl–Cl distance is 2.92A for 25°C and 2.9A for −20°C. These values are to be compared with the values of 1.85A and 2.95A obtained by Eisenstein.[4]

Assuming the known tetrahedral structure of the CCl_4 molecule in the gaseous state, the areas under the C–Cl and the Cl–Cl peaks should be $638e^2$ and $3610e^2$, respectively, whereas in the present work, the C–Cl areas are $620e^2$ for −20°C and $750e^2$ for 25°C; and the Cl–Cl areas are $3740e^2$ for 25°C and $3950e^2$ for −20°C. Since the corresponding peaks as shown by Eisenstein[4] are not discrete, it is difficult unambiguously to assign areas to them, though reconstructed peaks represent roughly $775e^2$ and $4129e^2$.

In previous work of this sort on liquids which are not monatomic, discrete peaks have been obtained in almost every case, and it is to be expected that this should also be true for CCl_4. Thus, discrete peaks were observed for the liquids phosphorus,[6] oxygen,[7] nitrogen,[8] chlorine,[9] sulphur,[10] nitric oxide,[8] nitrous oxide,[8] methyl alcohol,[11] and ethyl alcohol.[3] Only in the cases of methyl alcohol at 25°C and sulphur at high temperatures were the first distribution peaks not discrete for every one of these molecular liquids. But it has been pointed out that in these cases, the interatomic bonds are subject to rupture at high temperature. It is unlikely that the thermal motion of the atoms within the CCl_4 molecules could be great enough to give rise to distribution peaks which are not discrete.

The exact form of the distribution curve for CCl_4 is known to be strongly dependent upon the exact determination of the full form of the intensity curve and upon the fitting of the intensity curve to the independent coherent

[5] L. O. Brockway, Rev. Mod. Phys. **8**, 231 (1936).

[6] C. D. Thomas and N. S. Gingrich, J. Chem. Phys. **6**, 659 (1938).

[7] P. C. Sharrah and N. S. Gingrich, J. Chem. Phys. **10**, 504 (1942).

[8] P. C. Sharrah, Ph.D. Thesis, University of Missouri, Columbia, Missouri (1942).

[9] C. C. Gamertsfelder, J. Chem. Phys. **9**, 450 (1941).

[10] N. S. Gingrich, J. Chem. Phys. **8**, 29 (1940).

[11] G. G. Harvey, J. Chem. Phys. **6**, 111 (1938).

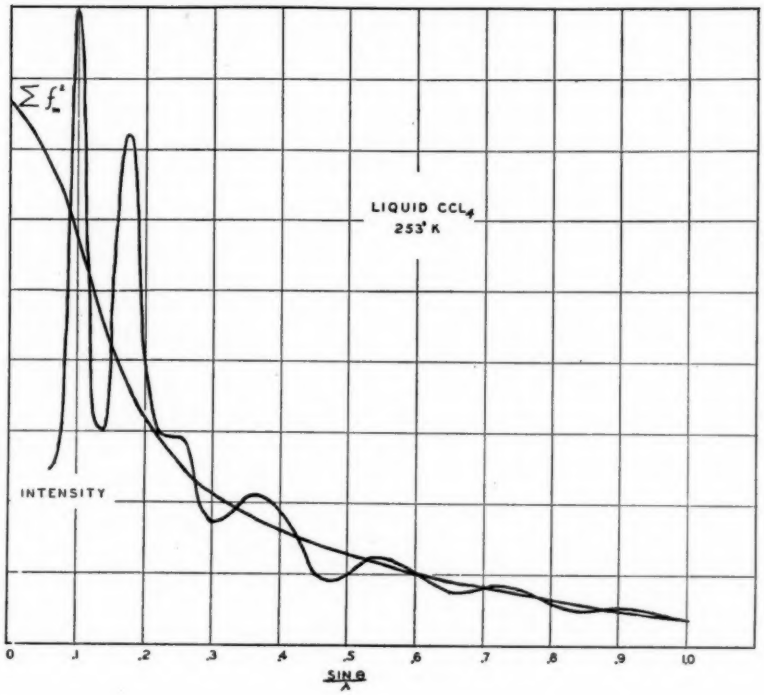

FIG. 2. Intensity pattern for liquid CCl_4 at 253°K, fully corrected and fitted to the independent coherent curve.

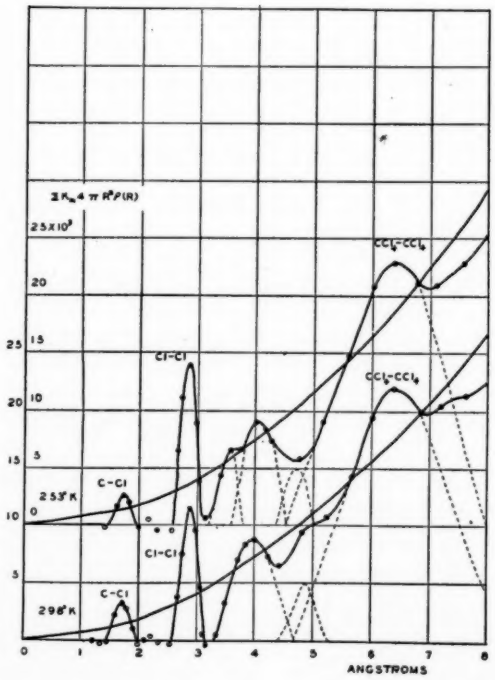

FIG. 3. Radial electron density distribution curves for liquid CCl_4 at 253°K and at 298°K.

curve. At 25°C, the use in the present work of a composite curve from over a dozen usable patterns should tend to make the final intensity curve quite reliable. The distribution curve shown for this case was the result of the one analysis made on the intensity curve for this temperature. At the lower temperature, −20°C, two separate fittings and analyses were made. Both gave two discrete peaks, at the positions labelled C–Cl and Cl–Cl, and the first analysis resulted in a small peak intermediate between these two. An average of the two analyses is presented in Fig. 3 which shows a vestige of this spurious peak.

Beyond the first two peaks, the prominences in the distribution curve undoubtedly arise from distances occurring between atoms in different molecules. None of these peaks is discrete, indicating that these distances are not fixed. Perhaps the best interpretation of the origin of these peaks can be given in terms of the explanation[12]

[12] C. A. Coulson and G. S. Rushbrooke, Phys. Rev. **56**, 1216 (1939).

for similar peaks found in the case of liquid phosphorus which also has a tetrahedral molecule. The peak near 6.4A represents the average distance between the centers of adjacent molecules, whereas the subsidiary peaks between about 3.5A and 5A represent frequently recurring distances between nearest approaching atoms in different molecules. The presence of peaks implies slight preferred orientations, probably due to valence saturation within the molecule, and a consequent slight repulsion between nearest chlorine atoms in different molecules.

In order to use the areas under reconstructed isolated peaks for determining the number of nearest-neighbor molecules, the areas under the subsidiary peaks should be included, as well as that under the large 6.4A peak, since these areas arise from parts of neighboring molecules. Furthermore, it seems clear that other and probably less well-defined peaks at distances greater than 6.4A should exist, to correspond to distances between atoms on opposite sides of adjacent molecules. Hence, the way in which the curve to represent the nearest neighboring molecules should be drawn in at distances greater than 6.4A is not well enough determined at present to obtain any reliable molecular coordination number. It is only possible to set a lower limit to this number. Following the contour of the distribution curves from about 3.2A up to about 6.8A, and then sloping off along the dotted line from there on, gives an area corresponding to a minimum number of nearest molecules. On the questionable use of the same type of area equation as was used for atomic scatterers, this leads to a coordination number of about five from the curves of Fig. 3. It is believed, however, that this number should be considerably higher in accord with the above interpretation of the significance of peak areas.

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The Magnetic Susceptibilities of Metals Dissolved in Liquid Ammonia

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(Received April 30, 1943)

Here are recorded data on the magnetic susceptibilities of potassium and of cesium dissolved in liquid ammonia at 240°K and 220°K. Also included are a few data on calcium and barium. These solutions throughout the entire range of concentrations were regarded as representing an electron gas. Such systems would permit the distributions of the magnetic moments of the electrons to be followed continuously from the degenerate region of the Fermi-Dirac statistics to those distributions where the quantum and classical statistics are indistinguishable. The general features of the magnetic behavior of a free electron gas were recognized, overlaid, however, by interactions characteristic of the environment of the electrons in the solutions. In the light of the magnetic susceptibilities as well as of other properties, a description is proposed for the structure of the solutions with special reference to the conduction electrons. Barium was found to dissociate into two electrons per gram atom and it is inferred that calcium dissociated likewise, but much greater dilutions would be required for a satisfactory demonstration. A method of considerable sensitivity and accuracy has been developed for measuring the magnetic susceptibilities of substances at low temperatures.

METALS dissolved in liquid ammonia have the property, primary for the present investigation, of dissociating into electrons and positive metal ions.[1]

In dilute solution, the conduction is electrolytic with the electrons as the negative ions carrying most of the current. The conductivity changes continuously with concentration and becomes metallic in the strong solutions. When saturated, a solution of sodium possesses about twice the conductivity of mercury at room temperature. Along with this behavior go changes in color which is a pale transparent blue in great dilution, deepens into a dense dark blue when more metal is dissolved, and acquires in concentrated solu-

[1] This classical work of Kraus is summarized by him in J. Frank. Inst. **212**, 537 (1931). Also in C. A. Kraus, *The Properties of Electrically Conducting Systems* (Chemical Catalog Company, New York, 1922).

tions a metallic bronze-like luster giving the solution every appearance of being a liquid metal. When the solvent is evaporated, the original metal is regained. In the case of lithium and also of calcium the metallic crystals which first deposit from the solution contain ammonia bound stoichiometrically, $Li(NH_3)_4$ and $Ca(NH_3)_6$. The former even at low temperatures dissociates into ammonia gas and the metal powder.

These phenomena speak strongly for regarding the solutions as a liquid metal whose concentration can be varied continuously over a great range. Like metals, the solutions may presumably be conceived as an electron gas which in better approximation is to be counted as subject to the microscopic fields in the solution.

The magnetic measurements were undertaken in order to follow the distribution in spin or magnetic moment among the electrons as a function of concentration and temperature. At high electron concentration, we would expect according to Pauli's well-known work[2] almost all the electrons to have paired-off their spins, the degenerate state of the Fermi-Dirac statistics, whereas in very dilute solutions, the elementary magnets would be independent of each other and conform to those distributions of the Fermi-Dirac statistics which are indistinguishable from the distributions of the classical statistics. To achieve a comparable variation in spin with the high electron densities prevailing in metals, it would be necessary according to theory to raise the temperature above the so-called degeneracy temperature, the order of 20,000°. By diluting the electrons of the metal, in our experiments with liquid ammonia, the degeneracy temperature would be greatly reduced, even considerably below the temperature where magnetic measurements are possible.

The degeneracy temperature is given by

$$T_0=\frac{h^2}{2mk}\left(\frac{3N}{8\pi V}\right)^{\frac{2}{3}},$$

where h is Planck's constant, m is the mass of the electron, k is Boltzmann's constant, N is the number of electrons in the volume V.

[2] W. Pauli, Zeits. f. Physik **41**, 81 (1927).

In a previous work,[3] it was shown that in its general features, the course of the variation of the susceptibilities was consistent with this outline. When sodium was at a concentration $0.5M$, its atomic susceptibility was of the same order of magnitude as that of the bulk metal. The degeneracy temperature for this concentration was about 2000°K, ten times higher than the temperature of the substance 230°K and, hence, the electrons were degenerately distributed. At

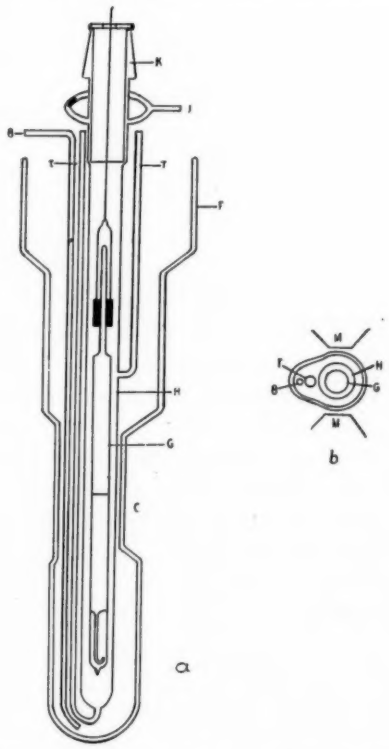


FIG. 1. Apparatus for measuring magnetic susceptibilities of substances at low temperature.

$0.002M$ with the degeneracy temperature at about 50°K, the atomic susceptibility had increased about one hundred fold and had attained values expected of an electron gas according to classical statistics.

These results were confirmed in the more extensive investigation of Huster and Vogt.[4,5] However, the data lacked the precision required for interpretation, especially in very dilute solutions where the actual forces to be measured were

[3] S. Freed and H. G. Thode, Nature **134**, 774 (1934).
[4] E. Huster and E. Vogt, Physik. Zeits. **38**, 1004 (1937).
[5] E. Huster, Ann. d. Physik **33**, 477 (1938).

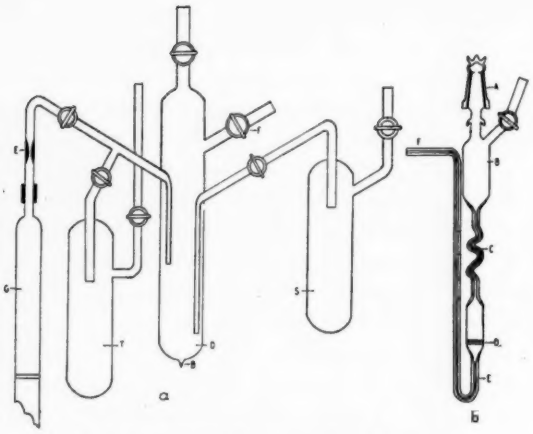


FIG. 2. Apparatus for preparing solutions of metals in liquid ammonia.

extremely small. Since the atomic susceptibility of sodium proved to have less than the theoretical value, the measurements had to be pushed to extreme dilutions in order to discover the limiting susceptibility. For this reason, we turned to solutions of potassium whose electrons would supposedly be "freer" than those of sodium; the conductivities at the same concentrations were known to be consistently higher. The susceptibilities were actually found greater and a satisfactory precision was obtained in the measurements. Also included in this communication are susceptibilities of solutions of cesium, of barium, and of calcium.

EXPERIMENTAL

Apparatus

A refinement[6] of the Gouy method of measuring magnetic susceptibilities was made available for substances at low temperatures without appreciable decrease in accuracy.

A vertical tube divided into equal sections by a horizontal partition is suspended from the arm of a microbalance so that the partition comes into the center of the pole gap of a magnet. One-half of the tube is filled with the solution and the other with the pure solvent. Under these conditions the susceptibility of the dissolved substance per unit volume in dilute solution is given directly by

$$K = K_{\text{solution}} - K_{\text{solvent}} = \frac{2F}{A(H_1^2 - H_2^2)},$$

where K is the specific volume susceptibility of the solution minus that of the solvent, F is the vertical force exerted on the balance arm, A is the cross-sectional area of the tube, H_1 is the field strength at the partition, while H_2 is that at the ends of the tube. In the more concentrated solutions, account must be taken of the fact that the solvent material in unit volume of the solution is not identical in amount with that in unit volume of pure solvent. This correction is usually small and altogether negligible in the more dilute solutions.

To extend the usefulness of this procedure for substances at low temperatures, the method consisted in suspending the glass tube G (Fig. 1a) in an atmosphere of stagnant hydrogen inside a tube H which was kept at the low temperature by the surrounding refrigerant liquid. A stream of dry hydrogen entered the stationary tube H at the upper end J and flowed to the outside atmosphere at such a rate as to keep the air with its moisture from descending during the experiment and affecting the weight of the tube G. Baffles with small openings could be mounted horizontally on the ends of the tube K which was perforated to allow easy entry of the hydrogen from the tubes J. The refrigerant, liquid ammonia, was kept in the Dewar vessel F. Its cap, not shown, was provided with connections to a manometer and pump for reducing the pressure and consequently the temperature of the refrigerant. The tubes T, T contained single junction thermocouples which abutted into H. The temperatures at the different levels of the hydrogen atmosphere as read by the thermocouples rarely varied by more than one-half degree even under unfavorable conditions. B was a capillary tube for the passage of air into the liquid ammonia to lessen the bumping of the liquid while it was being pumped.

The Dewar vessel F had a circular cross section with exception of the region C (Fig. 1b). This fitted into the pole gap and was therefore designed to separate the pole pieces as little as possible and yet accommodate the tubes T and B. The cylindrical tubing had been here enlarged on one side by means of a carbon form pressing out the glass while it was heated and softened without affecting the diameter of the circular portion.

G contained a trap at the lower end as shown

[6] S. Freed and C. Kasper, Phys. Rev. **36**, 1002 (1930).

(Fig. 1a). By this means the bubble of ammonia gas occupying the space left between the liquid and seal would not rise to the partition when the tube was inverted to its normal position for weighing. The liquid in *G* extended, then, in an unbroken column except for the horizontal glass partition.

Calibration and Measurement

The Gouy method for determining susceptibilities requires three measurements of force, a blank run on the container, a calibration with a substance whose absolute susceptibility is known, and finally the measurement of the material of interest.

Both portions of *G* were filled with liquid ammonia for the blank run. Ideally under these conditions the force would be zero but since the system was not perfectly symmetrical small correction forces were to be expected. The dissymetry due to the temperature gradient was so small that it was ignored. The extreme variation in the forces was as a rule not more than ± 0.003 mg from day to day. Pure liquid ammonia served for the calibration. Its susceptibility had been determined within an accuracy of one to two percent by Huster. The relative susceptibilities of the solute as measured by the present method were practically independent of the value accepted for the susceptibility of liquid ammonia. The absolute value was, however, determined by it.

For the calibration, the upper part of the tube *G* was filled with liquid ammonia, the lower portion was left evacuated and the net force noted on the balance at definite field strengths, i.e., definite currents in the electromagnet. The computations were made here as well as in all the measurements at 15.0 amp. with the corresponding field at about 15,000 gauss. The value at 15.0 was taken from a graph of forces against current. Although the individual points, in the measurements of the solutions, differed from the average by as much as 0.005 mg, it was found that in a twenty-four hour period, this average did not change by more than ± 0.002 mg. This variation together with that of the blank produced a probable error of ± 0.005 mg in the net force.

The tube factor defined as the ratio of the susceptibility to force changed less than 1 percent over the temperature range -33°C to -53°C.

At lower temperatures, the weighings were somewhat less accurate. When the bath was pumped to obtain lower temperatures, the ammonia bumped. This was almost entirely eliminated by aspirating air through the capillary tube *B*. To obtain a uniform temperature throughout the refrigerating liquid it was found necessary to heat the bath slightly throughout its length, a function performed with bare platinum resistance wire. In this manner, the temperature of the bath could be controlled to better than a degree with a temperature difference of less than one-half degree between the top and bottom.

Preparation of Solutions

Potassium and Cesium

The solutions were prepared in an all glass vacuum line system adapted by H. G. Thode and R. P. Metcalf of this laboratory from the procedures developed by Kraus and by Gibson and Phipps.[7] The metal was introduced into *D* at the point *B* (Fig. 2a) by distillation. A length of capillary had been filled with the metal and a section of the appropriate length was broken off for each concentration. The desired amount, within ten percent, was slowly distilled into *D* by the use of free flame. Ammonia which had been twice dried over potassium was condensed into *D*. The condensation was complete after there was enough solution in *D* above the upper siphon so that *G* could be filled and an aliquot portion of the remainder could be siphoned into *T*. The solution was then stirred by creating a slight vacuum and so bringing about vigorous boiling. The solution was then successively siphoned into *G*, *T*, and *S*. *G* was sealed off at *E* and the solutions in *T*, *S*, and *D* were kept for analysis.

Calcium and Barium

Because of the high melting points of these metals, another method was devised for introducing them into *D*.

TABLE I. Susceptibilities per gramatom χ_A.

Moles liter	Force (corrected) (mg)	K soln $-K_{NH_3}$ $\times 10^6$	$\chi_A \times 10^6$	Free electron gas $\chi_A \times 10^6$
		Potassium 240°K		
0.00341	0.123	0.00432	1268	1530
0.00384	0.127	0.00452	1180	1525
0.00406	0.152	0.00505	1240	1522
0.00481	0.160	0.00570	1180	1520
0.00812	0.222	0.00790	974	1505
0.00960	0.246	0.00819	853	1480
0.0318	0.359	0.01280	402	1060
0.482	1.126	0.0390	29.9	310
		Potassium 220°K		
0.00354	0.078	0.00286	809	1630
0.00422	0.100	0.00332	790	1620
0.00501	0.118	0.00417	834	1600
0.00844	0.116	0.00411	488	1550
0.0331	0.213	0.00765	232	1220
0.500	0.558	0.0194	−7.7	310
		Cesium 240°K		
0.00415	0.139	0.00470	1130	1500
0.00582	0.214	0.00724	1245	1480
0.00690	0.207	0.00700	1013	1460
		Cesium 220°K		
0.00432	0.096	0.00325	755	1620
0.00605	0.183	0.00618	1020	1580
0.00718	0.139	0.00472	657	1560
		Calcium 240°K		
0.00244	0.077	0.00274	1140	3060
0.0100	0.145	0.00531	938	2840
		Calcium 220°K		
0.00255	0.069	0.00245	978	3300
0.0105	0.079	0.00283	271	3040
		Barium 240°K		
0.00106	0.066	0.00235	2280	3400

[7] G. E. Gibson and T. E. Phipps, J. Am. Chem. Soc. **48**, 312 (1926).

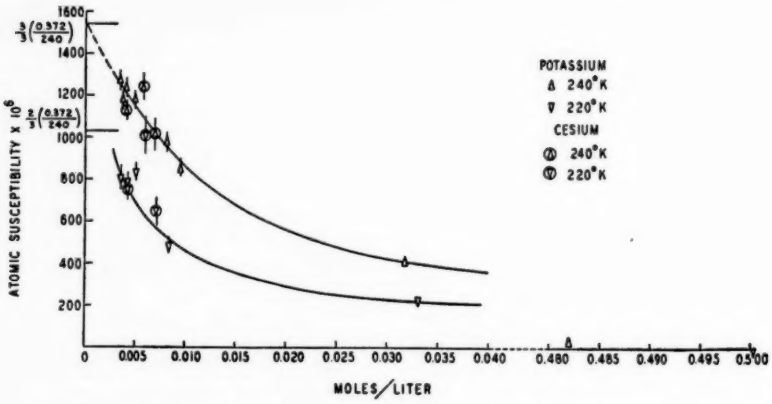


FIG. 3. Atomic magnetic susceptibility as a function of concentration.

The apparatus represented in Fig. 2b was sealed onto the vacuum line; *F* was joined to *F* on *D* (Fig. 2a). After the system had been thoroughly pumped, flamed, and flushed with gaseous and liquid ammonia, a piece of the metal was put into *B* and the system highly evacuated. Ammonia was then condensed on the metal so that the saturated solution which formed ran down the spiral capillary tubing *C* and through the filter plate *D*, a 01 Selas clay filter. This solution was siphoned into *D* through the stopcock *F*.

Analyses of Concentrations

The volumes of the solutions contained in traps *S*, *D*, and *T* were determined by distilling the ammonia into three measuring cells of the type described by Kraus.[8] After the ammonia had been distilled from *S*, *D*, and *T*, the residue was dissolved in water, boiled to remove ammonia and titrated with 0.01*N* HCl. The concentrations of the solutions in *D* were usually about 5 percent higher than those in *T* and *S* which agreed with each other within better than 1 percent. The higher concentration in *D* was doubtless due almost entirely to some undissolved metal which had condensed during the distillation considerably above the solution line. Because of good agreement in the analyses of the solutions in *T* and *S* and because siphonings were rapid, the concentration was taken as the average in *T* and *S*. In a few instances, *D* was averaged in if some mishap occurred to one of the other.

Previous work[9–11] has shown that the densities of the dilute solutions were practically identical with that of pure ammonia. Only in the most concentrated solution of potassium is the difference appreciable and the correction was applied. The actual density was obtained by interpolation from the data of Johnson and Meyer.

The experimental errors were incurred almost solely through the errors in weighing; the errors in analyses were relatively small.

[8] C. A. Kraus, J. Am. Chem. Soc. **43**, 749 (1921).
[9] C. A. Kraus, E. S. Carney, and W. C. Johnson, J. Am. Chem. Soc. **49**, 2206 (1927).
[10] W. C. Johnson and A. W. Meyer, J. Am. Chem. Soc. **54**, 3621 (1932).
[11] E. Huster, Ann. d. Physik **33**, 477 (1938).

The errors in the analyses of potassium and of cesium amounted to less than 1 percent, in calcium 2 percent, in barium 3.5 percent.

EXPERIMENTAL RESULTS AND DISCUSSION OF DATA

The data for the four metals measured are gathered in Table I and are also presented in the graph (Fig. 3).

The following features of the data support the idea held at the beginning that the solutions may be taken to represent an electron gas.

(1). In great dilution, the atomic susceptibility approximates the value which would arise from independent elementary magnets possessing one-half unit of spin.

(2). The concentrated solutions which obviously possess strongly metallic properties furnish atomic susceptibilities in rough agreement with the presence of an electron gas free to move throughout the volume. For example, Huster found that a saturated solution of sodium had an atomic susceptibility of about 80×10^{-6} whereas a free electron gas in the same volume would have about 40×10^{-6}.

(3). With increase in atomic volume, the atomic susceptibility increased. At 240°, the concentration where the steep increase sets in occurred at about 0.01*M*. The ideal theory has 0.02*M* as the concentration where the degenerate gas begins to pass into the classical distributions at 240°K. With increasing temperature, Fig. 3 indicates, the difference between the corresponding concentrations diminishes.

It is evident that the model of a free electron

gas must be extended to include interaction with the environment. Free electrons would because of their motion in a magnetic field show a diamagnetism[12] cancelling one third of the spin magnetism. The data establish that such a cancellation does not occur; the two-third value of the spin paramagnetism indicated by the lower horizontal line on the left of the graph is exceeded and the susceptibilities continue toward the full value due to spin, the upper horizontal line. Peierls[13] has raised the question whether Landau's conclusions are valid for a condensed system where the average frequency of collisions between the electrons and their environment is high.

The actual susceptibilities are in general lower than computed[14] for a free electron gas (last column of Table I) and even more drastic departure from such a model comes to light in the temperature dependence of the susceptibilities which decrease rather than increase with decreasing temperature.

To account for such a behavior, the idea naturally suggests itself that electrons are removed by the positive ions to form diamagnetic potassium molecules

$$2K^+ + 2E^- \rightleftarrows K_2.$$

It should be noted that the formation of potassium atoms or of molecular ions would instead increase the susceptibilities. Huster had assumed the presence of diatomic molecules in solutions of sodium. A computation shows, however, that the concentration of the molecules needed for agreement with the susceptibilities appears in conflict with the molecular weight of dissolved sodium as revealed by Kraus'[15] measurements of vapor pressures. There are other factors too which indicate that the hypothesis of dissolved diatomic molecules is rather forced. The very dilute solutions and the very concentrated solutions both are in agreement with a system consisting only of electrons and separate ions. The existence of the metals such as $Li(NH_3)_4$, $Ca(NH_3)_6$, $Sr(NH_3)_6$, $Ba(NH_3)_6$ containing the same number of ammonia molecules as completely surround the positive ions in their salts indicates strongly that the ions are separated from each other in these metals by ammonia. We shall take the single point of view that throughout the entire range of concentrations all these solutions consist of positive ions and electrons in ammonia and that no appreciable concentration of diatomic linkage exists between metal atoms or ions. We shall then inquire into the disposition of the conduction electrons to which the lower susceptibilities may be ascribed.

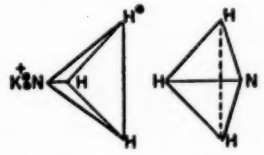
The specific volume susceptibility of a degenerate gas is given by[16,17]

$$K = 2\mu^2 (dZ/dE)_{E=E_0},$$

where K is the susceptibility per unit volume, μ is the Bohr magneton, and $(dZ/dE)_{E=E_0}$ is the number of energy levels per unit energy range at the top of the Fermi distribution. The energy of interaction of the magnetic moments of the electrons with the external field serves to uncouple the pairs of electrons in the filled cells and send some into empty ones so that the spins are in line. The effectiveness of this process depends upon the number of cells (or levels) which are available to the energy of interaction. Therefore, the more widely separate are the levels, the lower is the susceptibility.

It has been shown by Bardeen[18] that when resonance energies are included the resulting decrease in the density of levels lowers the magnitude otherwise computed for the heat capacity of metals. Magnetic susceptibilities are affected in the same general way.

This resonance binding may, we propose, be represented as follows:



solvated ion solvent

where the ammonia near the K^+ corresponds to

[12] L. Landau, Zeits. f. Physik **64**, 629 (1930).
[13] R. Peierls, Zeits. f. Physik **80**, 763 (1933).
[14] N. F. Mott, Proc. Camb. Phil. Soc. **32**, 108 (1936).
[15] C. A. Kraus, J. Am. Chem. Soc. **30**, 1197 (1908).
[16] W. Pauli, Zeits. f. Physik **41**, 81 (1927).
[17] W. F. Mott and H. Jones, *Theory of Properties of Metals and Alloys* (The Clarendon Press, Oxford, 1936), p. 184.
[18] J. Bardeen, Phys. Rev. **50**, 1098 (1936). See, e.g., F. Seitz, *Modern Theory of Solids* (New York, McGraw-Hill, 1940), p. 421.

one of the molecules of solvation and the ammonia structure facing it represents the solvent, in general, but may also on occasion stand for ammonia of solvation of another potassium ion. Structures with the electron near one of the hydrogen atoms may be imagined stabilized by the many equivalent or nearly equivalent structures which the situation may assume. The mobility of the electron in electrolysis may be viewed as the passage of the electron from one hydrogen atom to another with some differentiation between the ammonia molecules of solvation and of solvent.

Also contributing to the decrease in susceptibility and especially to its decrease with the temperature is the interaction of pairs of electrons which have some resemblance to F' centers known in systems composed of a metal such as potassium dissolved in a crystal as potassium chloride. In a site where a negative ion is missing, two electrons can lodge with some stability.[19] This pair is probably diamagnetic. In addition to the interaction having analogy with F' centers, the electron pairs are further stabilized through resonance in the same way as the unpaired electrons.

In our present schematization another electron would be attached, let us say, to one of the hydrogen atoms on the ammonia molecule to the right. The interaction of these electrons to form a diamagnetic pair would then account for the decrease in paramagnetism. Here again the electrical conductivity would be ascribed to the quantum mechanical passage through barriers somewhat as Farkas[20] assumed in an oversimplified model. In this way there appears no contradiction with the molecular weights as derived from vapor pressure measurements.

With further increase in electron concentration, the increased interaction may be viewed as an increase in the Fermi zero-point energy which operates to oppose the local trapping within barriers. Such a process is consistent with the gentle increase in susceptibilities at still higher concentrations which Huster found.

The lower susceptibilities of sodium compared with potassium (or of calcium compared with barium) may be linked chiefly to the relative sizes of these ions. The smaller ion induces a greater polarization in the ammonia of solvation with more positive charge localized on the hydrogen atoms. Relative to these hydrogen atoms, the exchange energies are increased with consequent decrease in the density of energy levels. Associated with this influence lowering the susceptibilities there is another aspect—the deepening of the energy barriers would favor an increased stability and concentration of the electron pairs.*

The fact that the atomic susceptibility of barium is definitely greater than that arising from one electron per gram atom is sufficient evidence that the ion dissociates into two electrons per gram atom which interact of course, with their environment. It appears highly probable that calcium dissociates in the same way but, as would be expected, the interaction is greater.

We wish to express here our gratitude for much assistance to Dr. Richard P. Metcalf and to Dr. Warren C. Johnson whose knowledge of the properties of liquid ammonia systems was always at our disposal.

[19] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (The Clarendon Press, Oxford, 1940), p. 128.
[20] L. Farkas, Zeits. f. physik. Chemie **A161**, 355 (1932).

* In a structureless medium, one expects on purely electrostatic grounds that the pairing of electrons would also take place to a greater degree with smaller ions. The Debye-Hückel ion atmosphere is here replaced by the electron atmosphere and with increased electrostatic potential from the smaller ion, there would be a greater probability of having more than one electron at a given distance from the center of this ion.

Infra-Red and Raman Spectra of Polyatomic Molecules XVIII. Trideuteronitromethane

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(Received April 15, 1943)

The infra-red spectrum of trideuteronitromethane has been studied in the range 3–25μ, and the Raman spectrum has been analyzed. From this data and that obtained by Wells and Wilson on nitromethane it has been possible to determine all the fundamental frequencies except that of the torsion about the C–N bond, and to carry out a normal coordinate treatment from which a potential function fitting the observed frequencies of nitromethane and trideuteronitromethane within 2 percent has been obtained.

AS pointed out by Wells and Wilson[1] the recent growth in industrial importance of nitromethane and other aliphatic nitro compounds has made their thermodynamic properties a matter of some interest. It was in hopes of obtaining a potential function for the nitro group in nitromethane which might be transferable to other members of this series that this investigation was undertaken. Such a set would permit *a priori* calculation of the nitro group frequencies for a statistical calculation of the thermodynamic properties of these compounds.

EXPERIMENTAL

Preparation of CD_3NO_2

The nitromethane used as a starting material was part of the same sample as that on which Wells and Wilson[1] performed their experiments. It had been specially purified and presented them by the Commercial Solvents Corporation.

Trideuteronitromethane was prepared from this nitromethane by a slight modification of the procedure developed by Reitz.[2] His method is essentially simply an exchange reaction with D_2O. An acetate buffer is used to prevent side reactions and the exchange is carried out at *ca.* 80°C to increase the rate of reaction.

In this particular case it appeared desirable to prepare 5–10 cc of material fairly high in deuterium content, so Reitz's experimental method, which involved use of a large excess of D_2O, was not employed. Instead the exchange was carried out using approximately equal weights of D_2O and CH_3NO_2.

The experimental procedure used here was as follows. For the first exchange 5 cc of 95 percent D_2O, 25 mg of c.p. sodium acetate and 0.01 cc of c.p. glacial acetic acid were added to 5 cc of CH_3NO_2 contained in a Pyrex tube. This tube was then stoppered (glass) and shaken on a combination shaker-oven for 20 hours at 75–80°C, after which the mixture was vacuum distilled through a drying tube containing "Drierite" and collected in a tube similar to the first reaction vessel. Since it was found that the distillation removed the acetic acid as well as the water, in order to start a second exchange fresh D_2O and the components of the buffer were added to the sample collected and the process above repeated. Between distillations the used D_2O was recovered by heating the $CaSO_4$ in a current of dry air, collecting the water in a dry ice trap.

Losses of nitromethane were rather high in these experiments, running nearly ½ cc per distillation by the above method. Later work by Dr. H. D. Noether[3] showed that considerably smaller losses were experienced when the distillation is carried out at reduced pressure in a current of air as recommended by Reitz.[2] The nitromethane lost, together with at least part of the acetic acid was recovered on regenerating the "Drierite" so the D_2O collected was badly contaminated. Most, if not all, of the impurities could, however, be removed by distillation from

* Present address: The Kellex Corporation, Jersey City, New Jersey.

[1] A. J. Wells and E. B. Wilson, Jr., J. Chem. Phys. **9**, 314 (1940), hereinafter referred to as XIII.

[2] O. Reitz, Zeits. f. physik. Chemie **A176**, 363 (1935).

[3] H. D. Noether, J. Chem. Phys. **10**, 664 (1942).

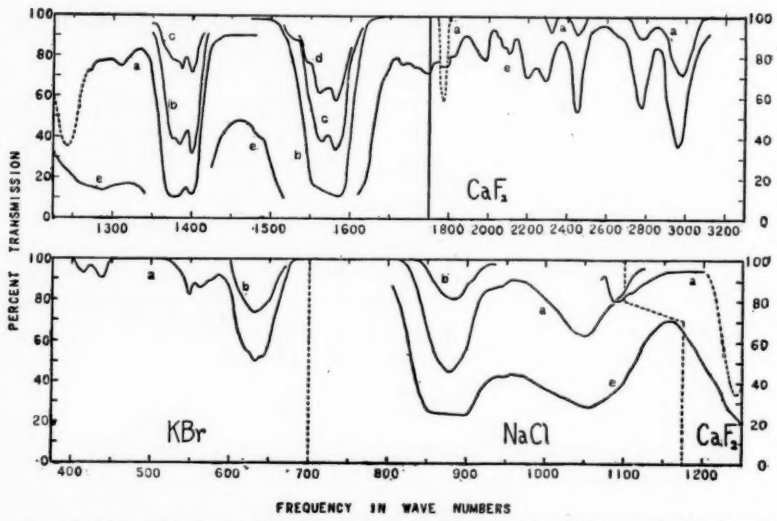

FIG. 1. Infra-red absorption spectrum of trideuteronitromethane. Bands drawn with broken lines in (*a*) are bands of the impurity (reference 3). Pressures of CD_3NO_2: (*a*) 30.5 mm; (*b*) 8 mm; (*c*) *ca.* 1 mm; (*d*) *ca.* 0.2 mm; (*e*) (heated cell, temperature of sample tube = 75°C) *ca.* 320 mm.

Na_2CO_3 (anhydrous) if the temperature was not raised much above 30°C.

Two series of exchanges were run to prepare the CD_3NO_2 used in these experiments. In the first series 5 cc of CH_3NO_2 were used as the starting material and the exchanges were run, the first with 5 g 95 percent, the second with 5 cc 98.3 percent and the third with 5 g 99.5 percent D_2O. The second series was started with 10 cc of CH_3NO_2 and exchanges were carried out with (1) 5 g 95 percent, (2) 5 cc 98.3 percent, (3) 5 cc 98.3 percent, (4) 5 cc 98.3 percent, (5) 10 g 99.5 percent D_2O.

Deuterium Content and Purity of Product

Calculations of the deuterium content of the product were carried out using the distribution coefficient determined by Reitz:[2]

$$(D_n/H_n)/(D_w/H_w)=0.78$$

at equilibrium. Here

D = fraction of total places for hydrogen occupied by D,

H = fraction of total places for hydrogen occupied by H,

and the subscripts n and w refer to the nitromethane and water, respectively, present in the reaction mixture. After making some simplifying assumptions which should make the calculated values slightly low, assuming Reitz's constant holds for all deuterium contents, a value of D_n of 0.93 was calculated for the product of the first run and 0.95 for the product of the second.

Dr. W. D. Kennedy was kind enough to do a mass spectrographic analysis of a sample from a mixture of the end products of the two runs, 2 cc of the first and 7 cc of the second. His results indicated the presence of about 15 percent CHD_2NO_2. This corresponds to a value of $D_n=0.95$, indicating the calculations and the assumptions on which they are based were as nearly correct as expected. Such a high percentage of CHD_2NO_2 present in the sample might be expected to show up in the spectra.

The sample used in the investigation of spectra gave no test for water with anhydrous $CuSO_4$. The presence of some other impurity is, however, indicated by the appearance in the infra-red spectrum of bands which are not due to any of the isotopic species of CD_3NO_2. Dr. H. D. Noether[3] has succeeded in isolating this same impurity from his materials obtained from CD_3NO_2 prepared by the same process used here. For further information on this subject, the reader is referred to his paper.

Infra-Red Spectrum

As in the investigation of CH_3NO_2 in XIII it was necessary to use a heated cell to investigate

the weaker bands. A somewhat different type was, however, developed for use in this work since loss of sample was definitely undesirable. It was found that nitromethane had little or no effect on rubber when heated with it for several hours so cells were constructed having rubber gaskets between the NaCl windows and the 25-cm Pyrex tube to take care of the different coefficients of expansion which had caused windows to crack on cooling in previous cells where the window had been cemented directly to the tube. Flanged heated copper collars 2 inches in length were used to serve the dual purpose of supporting the windows and preventing the condensation of nitromethane on them. In order to avoid the use of excessive heat in maintaining the cell windows at the desired temperature dummy NaCl windows were supported on the outer ends of the collars to prevent free circulation of air. The inner metal flanges to which the collars were bolted were held in place by the flanged ends of the glass tube protected by rubber washers. When the entire assembly was bolted together the outside of the tube-gasket-window joint was sprayed with a 1 : 4 solution of red Glyptal in benzene to make a vacuum tight seal. After drying, and baking for twelve hours while pumping on the cell with an oil pump, it appeared to be satisfactorily tight. No trouble was experienced, in all the times that the cell was used, with windows cracking.

In operation of the heated cell, the sample was vacuum distilled into a trap on a side arm of the cell, which was then sealed off under vacuum. The pressure of nitromethane was regulated by adjusting the temperature* of an oil bath in which the trap was immersed. In this way the pressure was kept at a known value within an estimated probable error of about 20 mm. The temperature of the body of the cell, which naturally had to be kept hotter than the trap, was estimated from a calibration of heater current *versus* cell temperature obtained on the empty cell. Since no quantitative measurements were desired the 10–15°C probable error was not considered important.

* The vapor pressure-temperature data on CH_3NO_2 [see E. B. Hodge, Ind. Eng. Chem. **32**, 748 (1940)] was used in the absence of such information on CD_3NO_2. The difference is slight at temperatures both higher and lower than those used in this work.

Cells used in the room temperature work were the usual 30-cm Pyrex tubes with NaCl or KBr windows held in place with clear Glyptal or Duco which have been used in previous investigations in this series.

The automatic prism spectrometer used in these investigations has been described in I[4] of

TABLE I.

Infra-red		Raman	
Frequency (cm^{-1})	Intensity	Shift* (cm^{-1})	Intensity and polarization
2940	2	3018 (*e*)[a]	½
2765	1		
2442	1		
2290	½	2300 (*e*, *k*)	3 (broad)
2195	½	2189 (*e*, *k*)	4 (*P*)**
2107	+	2116 (*e*, *k*)	3 (*P*)
2064	+	~2065 (*e*, *k*)	1 (*P*)
1992	+		
1820	+		
1785	+		
1763	+		
1696	+		
1668	+		
1581 1562	20	1544 (*e*, *k*)	4
1545?	1		
1527	1		
1398 1384 1376	15	1390 (*e*, *f*, *i*, *k*, *g*)	7 (*P*)
1310	2		
~1276	2	~1250[a] (*e*, *k*?)	½ (*P*)
1090	½	~1079 (*e*, *k*?)	3 (*P*)
1051	5	1041 (*e*, *k*)	3−
~1000	1		
944	2		
879	10	895 (±*e*, *f*, *g*, *i*?, *k*)	6 (*P*)
632	4	627 (±*e*, *i*, *k*)	5 (*P*)
578 563 547	½ 1 2	544 (±*e*, *i*?, *k*)	1+
436 412	1	433 (±*e*, *k*)	2+

[a] See text.
* The letters in brackets following the frequencies of the Raman shifts indicate the exciting lines in the Hg spectrum from which these shifts were observed. Kohlrausch's nomenclature is employed.
** (*P*) indicates that the line so marked is noticeably polarized. Other lines are apparently depolarized.

[4] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938).

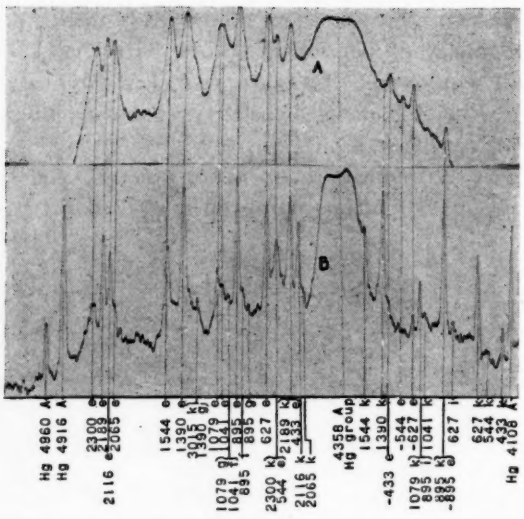

FIG. 2. Microphotometer traces of CD_3NO_2 Raman spectra. (A) Taken with Wratten No. 2*A* around the Raman tube and 0.09 g/l of Rhodamine 5 *GDN* extra in the coolant. (B) Taken with Polaroid polarizing light incident on the Raman tube perpendicular to its axis.

this series. The calibration was accomplished by observations on the appropriate bands in CO_2, C_2H_2, C_2H_4 and CH_3Br. The CaF_2 prism was used in the range 3–9μ, the NaCl prism from 8 to 16μ, and the KBr prism from 14 to 25μ. Figure 1 shows the spectra obtained at various pressures, and the positions of the absorption maxima, together with their relative intensities as estimated visually from the curves obtained, are listed in Table I. The fact that the overlapping curves taken with the NaCl and CaF_2 prisms in the 1100 cm^{-1} region do not coincide is due to the much greater resolving power of the latter there.

The low intensity of the absorption due to the C–D stretching vibration is immediately evident. Considering the presence of the stronger bands at 2765 and 2940 cm^{-1}, one might be inclined to question the reported deuterium content if it were based only on calculations. The other evidence presented supports the calculations, however, and makes it appear likely that the higher frequencies mentioned are combinations.

Raman Spectrum

The investigation of the Raman spectrum was carried out using the spectrograph described by Gershinowitz and Wilson[5] and qualitative polarization data were obtained by the "Polaroid" method.[6] On some plates a Wratten No. 2*A* gelatin filter wrapped around the Raman tube was used to eliminate excitation by the 24335 (*h*), 24516 (*i*), and 24705 (*k*) cm^{-1} Hg lines and Rhodamine 5*GDN* extra was used to eliminate the green Hg lines as described in XIII. Cu comparison spectra were taken on each plate. Table I gives the observed shifts together with the exciting lines from which the shifts were observed, an estimate of the relative intensities and indication of whether or not the shift is appreciably polarized. Figure 2 shows microphotometer traces of two Raman plates, one taken without Polaroid and the other with the incident light polarized perpendicular to the axis of the Raman tube.

In this spectrum the 2200 and 2300 cm^{-1} frequencies show up quite strongly as expected. The 3018 cm^{-1} shift observed on the stronger plates is probably attributable to the CHD_2NO_2 known to be present, although it is possible that it is due to the impurity.[3] Absorption bands of the impurity were observed at 3000, 1760, and 1240 cm^{-1} and a weak 1250 cm^{-1} shift was observed in this spectrum. The observed shift is probably not a combination of CD_3NO_2 frequencies since resonance with a fundamental appears unlikely.

Other than the possibility of a very weak polarized 980 cm^{-1} shift, the remaining lines observed are readily assigned to CD_3NO_2.

THEORETICAL

Assignment of Fundamentals

As in XIII nitromethane is treated as having the symmetry C_{2v}, using the theory developed by Crawford and Wilson.[7] The selection rules of this group permit the appearance in both Raman and infra-red of all the fundamentals except that due to torsion about the C–N bond which is inactive. Since they also permit the appearance of most of the combinations they are of little help in making an assignment.

[5] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 247 (1938).
[6] J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. **6**, 124 (1938).
[7] B. L. Crawford and E. B. Wilson, Jr., J. Chem. Phys. **9**, 323 (1941).

TABLE II.

Representation	Type of vibration	Frequency (cm^{-1}) Assigned CH_3NO_2[1]	Assigned CD_3NO_2	Calculated CH_3NO_2	Calculated CD_3NO_2	Product ratio[2,3] Theor.	Product ratio[2,3] Obs.
	C−H stretching	2965	2160	2965	2125		
	CH_3 bending	1413	1090	1426	1092		
A_1	N−O stretching	1384	1384	1363	1387	1.95	1.91
	C−N stretching	921	879	920	879		
	NO_2 bending	647	632	651	625		
A_2	Torsion about C−N	—	—	—	—	—	—
	C−H stretching	3048	2290	3046	2259		
	N−O stretching	1582	1571	1580	1561		
B_1	CH_3 bending	1449	1051	1480	1068	2.61	2.60
	CH_3 rocking	1097	~879	1101	866		
	NO_2 rocking	476	424	470	433		
	C−H stretching	3048	2290	3046	2259		
	CH_3 bending	1488	1051	1487	1066		
B_2	CH_3 rocking	1153	944	1161	936	2.50	2.46
	NO_2 rocking	599	560	601	561		

[1] A. J. Wells and E. B. Wilson, Jr., J. Chem. Phys. **9**, 314 (1940).
[2] O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).
[3] W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, J. Chem. Soc. 971 (1936).

The assignment of frequencies to the vibrations having the symmetry A_1 is readily accomplished by considering the polarization data on the stronger Raman lines. The 2189, 2116, and 2065 cm^{-1} shifts must be the symmetrical C−D stretching resonating with 2×1079 and 2×1041. By comparison with other molecules the 1079 cm^{-1} shift must be the symmetrical bending of the CD_3 group, but here, in contrast to the other Raman shifts, the value of the gas phase infrared frequency corresponding is not immediately evident for the 1050 cm^{-1} is not visibly split into two components as it is in the Raman spectrum. It is possible that the parallel and perpendicular bending frequencies show markedly different shifts in going from the liquid to the gas phase, but since the 2000–2200 cm^{-1} region remains practically unchanged on this transition (three lines at approximately 2190, 2110, and 2065 cm^{-1} in both spectra) it seems more probable that a difference still exists between the gas phase frequencies of the two types of vibration, and the 1090 cm^{-1} band observed using the fluorite prism has been somewhat arbitrarily chosen as the symmetrical fundamental. The assignment of the other symmetrical fundamentals requires no explanation.

TABLE III.

Spectrum	Observed	Assignment
Raman	~1250	2×627=1254?
	~2065	2×1041=2082
	2116	2×1079=2158
Infra-red	~1000[a]	560+424=984?
	~1276	2×632=1264
	1310	879+424=1303
	1527	944+632=1576?
	1545	879+632=1511
		~879+632≦1511
	~1696	1051+632=1683
		1080+632=1712
	1763	2×879 ($2A_1$, $2B_1$ and
	1785	A_1+B_1)≦1758
	1820	879+944=1823
	1992	1571+424=1995
		1051+944=1995
	2064	2×1051=2102
	2107	2×1090=2180
	2442	1571+ 879=2450
		1384+1090=2474
	2765	2×1384=2768
	2940	1571+1384=2955

[a] See text.

Most of the other fundamentals may be assigned frequencies on the basis of comparisons with other compounds containing analogous groups or from consideration of the mechanics of the vibrations. The broad line at 2290 cm^{-1} must be the unsymmetrical C−D stretching frequencies, since it is the only strong unpolarized Raman shift in that region. 1571 cm^{-1} is asso-

TABLE IV.

Constant	Value	Coordinates involved*
K_H	4.96×10^5 dynes/cm	Δr_i in CH_3
k_H	0.04	$\Delta r_i\cdot\Delta r_{i\pm1}$ in CH_3
H_α	0.46	$r_0(\Delta\alpha)$ in CH_3
$l_{\alpha\beta}$	0.01	$r_0(\Delta\alpha)\cdot r_0(\Delta\beta)$ in CH_3
$H_{\beta NO_2}$	0.665	$r_0(\Delta\beta)$ in H_3C-NO_2
$l_{\beta\beta}$	−0.035	$r_0(\Delta\beta_i)\cdot r_0(\Delta\beta_{i\pm1})$ in CH_3NO_2
$k_{N\gamma}$	−0.35	$r_0(\Delta\alpha_i)\cdot\Delta R$, $r_0(\Delta\beta_i)\cdot\Delta R$†
K_{RNO_2}	4.74	ΔR
K_{NO}	9.72	$\Delta\mathbf{R}$
k_{NO}	2.54	$\Delta\mathbf{R}_1\cdot\Delta\mathbf{R}_2$
k_{RNO}	0.636	$\Delta R\cdot\Delta\mathbf{R}$
H_γ	$2.263\times10^{-11}\frac{\text{dyne-cm}}{\text{(radians)}}$	$\Delta\gamma$
H_δ	0.404	$\Delta\delta$
$l_{\gamma\gamma}$	1.264	$\Delta\gamma_1\cdot\Delta\gamma_2$
$k_{\mathbf{R}\gamma}=k'_{\mathbf{R}\gamma}$	$-0.353\times10^{-3}\frac{\text{dyne}}{\text{radian}}$	$\Delta\mathbf{R}_i(\Delta\gamma_i)=\Delta\mathbf{R}_i(\Delta\gamma_{j\neq i})$
$k_{R\gamma}$	0.749	$\Delta R(\Delta\gamma_i)$

* The coordinates involved in calculations on the methyl group are those used in previous work (see reference 9 and 16). In the table above the nomenclature for the remainder of the molecule is as follows: R = C−N bond, $\mathbf{R}$ = N−O bond, γ = C−N−O angle, δ = angle between the C−N bond and the plane of the NO_2 group.
† See reference 16.

ciated with the NO_2 group and obviously is the unsymmetrical stretching frequency. We have assigned both the B_1 and B_2 CD_3 bending frequencies the value 1051 cm^{-1} since the 1000 cm^{-1} line, if present, is almost certainly too low, and the two are apparently not resolved in either spectrum.

The bands at 424 and 560 cm^{-1} may be assigned to the NO_2 rocking motions in B_1 and B_2, respectively, on the basis of the same moment of inertia of the NO_2 group arguments used in XIII. This assignment is checked by the observed band envelopes. From the moments of inertia and the envelopes published by Badger and Zumwalt,[8] using their method, it was found that in both compounds the B_1 bands should be doublets while the B_2 bands should have "Q" branches. In the latter case the "Q" branch should be considerably weaker in CD_3NO_2 than in CH_3NO_2. A comparison of the spectra of the two compounds shows this to be the case.

The least definitely established assignment of frequencies for this molecule is that for the two CD_3 rocking motions. Qualitatively one might expect that the frequencies should be split due to the difference in moments of inertia of the NO_2 group about the two axes as discussed in assigning the NO_2 rocking motions, and by the same argument used in that case the B_1 rocking should have a lower frequency than the B_2. It also might be predicted that both should be lower than 970 cm^{-1}, the value found for C_2D_6 by Stitt,[9] since the NO_2 group has a considerably greater moment in CD_3NO_2 than the CD_3 group has in C_2D_6. If, then, the doubtful infra-red band at 1000 cm^{-1} is eliminated on these grounds, and the 944 cm^{-1} infra-red band is assigned to the B_2 rocking motion, the other must be lower. No band or Raman shift is separated, but the lack of a definite envelope for the 879 cm^{-1} band indicates that it may actually be double. There seems to be no logical alternative to this selection on the basis of the evidence available at present and it is at least partially justified by the fit obtained with it when the product rule is applied. (See Table II.)

[8] R. M. Badger and L. R. Zumwalt, J. Chem. Phys. **6**, 711 (1938).

[9] F. Stitt, J. Chem. Phys. **7**, 297 (1939).

Table III gives a tentative assignment of the combinations appearing in the Raman and infrared spectra, on the basis of the above assignment of fundamentals. The doubtful band at 1000 cm^{-1} may be a combination if C_{2v} selection rules are violated, but it seems more likely that it is a low frequency branch of the 1051 cm^{-1} band, or it is due to an impurity.

Except for the slim possibility that the 1000 cm^{-1} band may be a combination involving it, there is no evidence as to the value of the torsional frequency in either of the spectra of CD_3NO_2.

The Vibrational Potential Function

In the calculations of moments of inertia to obtain band envelopes as well as those discussed in this section, the dimensions determined by Brockway, Beach, and Pauling[10] for CH_3NO_2 were used. These are

$$C-N=1.46\pm0.02A; \quad N-O=1.21\pm0.02A$$
$$O-N-O \text{ angle}=127\pm3°.$$

As in XIII we assume that $C-H=1.08A$ and that all the methyl group angles are tetrahedral.

We also make the usual assumption that neither the dimensions nor the potential function of the molecule is changed by substitution of D for H. The frequency shifts are then entirely due to mass differences. There is a slight difference in the anharmonicities of the C−H and C−D stretching vibrations and the deviation of the observed from the theoretical product rule ratios[11,12] is in the expected direction[13] and is believed to be due to this cause. In the case of the B_1 frequencies, where the observed deviation is smaller than expected from comparison with other cases, the difficulty probably lies in the 879 cm^{-1} rocking frequency which is hidden in the strong C−N stretching band. To obtain a better fit with the expected ratio the rocking frequency would have to be raised slightly, which would produce somewhat better agreement with the observed combination bands as well.

The normal coordinate treatment from which the potential function given in Table IV was obtained was carried out using methods previously described.[14,15] The secular equation was set up using the bond vector method and the high frequencies then split out.[14] It was not found possible to factor out the N−O stretches, but the C−H and C−D stretches were treated separately, the success of the treatment being indicated by the fit obtained with the observed frequencies.* The force constants given in Table IV for the C−H stretch were determined from the frequencies observed in CH_3NO_2 since work by Crawford and Brinkley[16] has shown that in CH compounds factoring out the C−H stretch introduces an error of only about 0.1 percent if no other frequencies in the molecule under consideration are above 2000 cm^{-1}. It might be expected that the approximation would not hold so well in a case such as CD_3NO_2 where the frequency factored out is around 2200 cm^{-1} and other frequencies in the molecule are as high as 1500 cm^{-1}. As shown in Table II, however, the error is only what would be expected from the anharmonicity of the C−H stretches. In comparison with the anharmonicity effect the error introduced by factoring out the C−D stretches appears to be negligible.

When the potential function given in Table IV is factored as indicated it reduces to the same form as that given in XIII for the B_1 and B_2 representations. As will be noted the fit obtained with the values of the constants reported here is not quite as good as that given in the previous paper, especially in B_1.** A better fit could undoubtedly be obtained by introducing more interaction terms, in particular one between the N−O stretch and the CH_3 bend, but since the agreement is probably good enough for most purposes and since the potential function in the two unsymmetrical representations treated has the

[10] L. O. Brockway, J. Y. Beach, and L. Pauling, J. Am. Chem. Soc. **55**, 2693 (1935).
[11] O. Redlich, Zeits. f. physik. Chemie **B28**, 371 (1935).
[12] W. R. Angus, C. R. Bailey, J. B. Hale, C. K. Ingold, A. H. Leckie, C. G. Raisin, J. W. Thompson, and C. L. Wilson, J. Chem. Soc. 971 (1936).
[13] O. Redlich, J. Chem. Phys. **7**, 856 (1939).
[14] E. B. Wilson, Jr., J. Chem. Phys. (*a*) **7**, 1047 (1939); (*b*) **9**, 76 (1941).
[15] M. A. El'yashevich, (*a*) Comptes rendus Acad. Sci., U.S.S.R. **28**, 604 (1940); (*b*) J. Phys. Chem. (U.S.S.R.) **14**, 1381 (1940); (*c*) Ibid. **15**, 831 (1941).
* See Table II.
[16] B. L. Crawford, Jr., and S. R. Brinkley, Jr., J. Chem. Phys. **9**, 69 (1941).
** This is due in part to a slight numerical error made in setting up the secular equation used in the work reported in XIII.

advantage of almost surprising simplicity, no attempt has been made to improve things except by changing the numerical values of the force constants involved.

In the A_1 representation the most general potential function, after factoring out the C−H stretches, would contain ten parameters. From the other representations it would appear that the interactions between motions of the NO_2 group and the CH_3 group should be small. For this reason the two parameters corresponding to such interactions were omitted. Interactions between the C−N stretch and the other motions are probably present.[16] The other interaction appearing in this representation is one between the N−O stretching and the NO_2 bending. In B_1 the corresponding interaction is apparently not important. When it was omitted, however, preliminary investigation showed that the values of the other constants necessary to fit the observed frequencies would probably be so widely divergent from those expected as to cast doubt on the validity of the potential function. By including the $\mathbf{R}-\gamma$ interaction it was possible to obtain the agreement between observations and calculations given in Table II and still keep values of the other constants somewhere near what was expected.* The $\mathbf{R}-\gamma$ interaction was chosen rather than either of the other two possible ones because it was felt that the charge on the nitro group might well lead to some interaction not accounted for entirely by "diagonal" valence type force constants.

It will be noted that while eight parameters have been adjusted in this representation, there are actually only seven independent conditions, for while there are eight frequencies the assumption of identical potential functions for the two molecules imposes one condition on them. The potential function given, then, is certainly not unique. It does fit the facts considered in obtaining it, but further tests, perhaps on other nitro compounds, should be made before a great deal of reliance is placed on it.

It is interesting to note that if the A_1 representation is excluded eighteen frequencies have been fitted with a maximum deviation of 2 percent by adjusting only five constants, taking the others necessary from Stitt's work on ethane.[9] At least in these particular cases the form of the potential function and the numerical values of the constants used is quite satisfactory.

The fact that it has proved possible, using a tetrahedral structure for nitromethane, to obtain a reasonable potential function which fits the observed frequencies of both CH_3NO_2 and CD_3NO_2 supports the view expressed in XIII that this is at least the form present in by far the largest amounts.[17] No frequencies appearing in either the Raman or the infra-red spectra of CD_3NO_2 require postulation of a second form.

In conclusion the writer would like to acknowledge his indebtedness to Professor E. Bright Wilson, Jr., not only for suggesting this problem and for his continued interest and many helpful discussions during the course of the investigation, but also for making available the original calculations on CH_3NO_2 by himself and Dr. A. J. Wells. I should also like to express my appreciation to Dr. Wells for permission to use his work and for his interest in this problem.

* By analogy with results from other compounds, it was expected that the C−N stretching constant, K_{RNO_2} = 4.0–5.5 dynes/cm; also $K_{N\gamma} = -0.3$ to -0.5 dyne/cm.

[17] See E. Pendl, A. W. Reitz, and R. Sabathy, Proc. Ind. Acad. Sci. **8**, 508 (1938) (Raman Jubilee Volume).

Infra-Red and Raman Spectra of Polyatomic Molecules. XX. Cyclobutane

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The infra-red spectrum of cyclobutane in the range 2 to 25μ has been obtained, together with the Raman spectrum of the same material. Analysis of these spectra, together with a normal coordinate treatment of the problem, has led to a tentative assignment of the fundamentals which explains all features of the observed spectra. Butene-1 has been identified as a product of the liquid phase photolysis of cyclopentanone.

THE vibrational spectrum of cyclobutane is of interest on several counts. It provides an example of a comparatively complex molecule of high symmetry in which there is no internal rotation. Also, according to the usual model, it is somewhat strained and there is a possibility of investigating the effect of this strain on the valence type force constants. Recently some question has been raised concerning the structure of hydrocarbon rings, so the structure of cyclobutane may require proof. There is also the possibility of using the spectrum obtained to calculate thermodynamic properties of this material.

Recent work[1] in these laboratories on the photolysis of cyclic ketones made it appear possible that this method could be used to prepare cyclobutane in small quantities somewhat more simply than it can be done using the method devised by Willstätter[2] and lately modified by Heisig.[3] This work was undertaken to test the practicability of the method of preparation as well as to investigate the spectrum of the product.

EXPERIMENTAL

Preparation of C_4H_8

As indicated above, the cyclobutane used was prepared by the gas phase photolysis of cyclopentanone in a manner similar to that described by Benson and Kistiakowsky.[1] Certain changes were made in the construction of the apparatus, however, in view of the fact that our primary interest was in only one of the products of decomposition, and as much as possible of that was desired.

Since it has been shown that the relative amounts of decomposition products are independent of temperature and pressure over the immediately available ranges, it appeared that the only way to increase the rate of formation of cyclobutane was to increase the intensity of illumination. The arc[4] used in the previous work is the most intense source of ultraviolet radiation with which we are acquainted, but in those experiments the light was not focused particularly well. We, therefore, enclosed the arc and quartz reaction tube in an elliptical stainless steel reflector, the arc at one focus, the tube at the other. An air blast had to be turned on the outside of the reflector to prevent its staining from the heat of the arc. Since the arc had to be mounted horizontally, the tube had to be similarly oriented.

An oven was used as before to keep the leads to the reaction tube hot. For simplicity in construction the reaction tube was also inside the oven, so about half the reflector was too. Actually no heat other than that from the arc was necessary to keep the reaction tube above the boiling point of cyclopentanone.

The quartz spiral manometer was eliminated since knowledge of the true pressure in the reaction chamber was unimportant. The mercury regulator on the other side of the condenser gave a sufficiently accurate measure. A thermocouple was used in preliminary experiments to determine very approximately the temperature inside the reaction tube.

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[1] S. W. Benson and G. B. Kistiakowsky, J. Am. Chem. Soc. **64**, 80 (1942).

[2] R. Willstätter and J. Bruce, Ber. **40**, 3979 (1907).

[3] G. B. Heisig, J. Am. Chem. Soc. **63**, 1698 (1941).

[4] Engineer's Bulletin No. 53, General Electric Company (Nov. 1939).

The system of taking off reaction products was also changed. The gases, after passing through the reaction tube, were fed into the center of a vertical condenser, the cyclopentanone condensing and running back into the pot while the products not condensable at 5–15°C collected above and leaked off through a mercury pressure regulator. Gas coming off through the regulator was passed through a trap in dry ice-acetone to remove residual cyclopentanone and any other high boiling substances which might be present, and then through a trap in liquid nitrogen to collect the cyclobutane and ethylene. CO was pumped out continuously with an oil pump. The photolysis and collection using this apparatus were completely automatic, once started.

The cyclopentanone used as a starting material was a combination of samples, for one of which we wish to thank Dr. J. J. Leavitt, of these laboratories, who presented it to us, the other from Eastman Kodak Company. It was purified by distillation, first through a small Widmer column (b.p. 129.1–129.3°C), then through a $3' \times 1''$ column with wire gauze (Purdue) packing at a reflux ratio of 30 : 1. The sample used had a constant boiling point of 129.2°C at 762 mm. It was stored in a black painted, tin foil wrapped flask attached to the line, and portions were vacuum distilled into the pot for the photolysis.

As in the previous experiments the reaction system was evacuated with a Hg pump before starting the photolysis. Runs were made at a pressure of 200–300 mm and temperature of 250°–300°C in the reaction tube.

For larger amounts of products than those obtained by Benson and Kistiakowsky,[1] simple vacuum distillation is a somewhat more convenient method of purification than that employed by them. We used this, carrying out the distillations at the temperature of solid CO_2.

Using the apparatus and conditions given above we were able to obtain about 0.1 cc of liquid cyclobutane per hour of operation at best. One of the factors limiting the rate of decomposition of cyclopentanone seemed to be the rate at which it was possible to distil it through the circulating system without producing bumping. Formation of a brown deposit, presumably a high polymer, on the walls of the reaction tube may also have cut down the effective radiation somewhat.

Purity of Product

Two lots of cyclobutane were prepared, one of which was used for preliminary infra-red work and the Raman spectrum, the other for final infra-red work and the spectroscopic investigation of impurities. The first had a vapor pressure range at −78°C of 4–8 mm. The second, after bromination, had a range of 4.5–7 mm at the same temperature (cf. 5.1 mm[3]).

Physical tests of the purity were run on the first batch. The tests used were the vapor pressure at various temperatures, the differential vapor pressure test[5] of purity and the vapor density (for both identity and purity of product).

Vapor pressure measurements at 0°C and −14°C showed the vapor pressure of the sample to be slightly above that for pure cyclobutane.[3] This was confirmed by differential vapor pressure measurements by Shepherd's method.[5] By this latter method it was estimated that 0.5 percent of ethylene was present, assuming that to be the only impurity. From measurements of the molecular weights at various pressures[6] of the first and last halves of an approximately isothermal distillation, assuming the impurity to be ethylene and the apparent molecular weight of cyclobutane to be a linear function of the pressure, a value of 0.35 percent ethylene was calculated. The measured molecular weights, when corrected for the presence of ethylene, plotted on a pressure scale and extrapolated to $P=0$, gave a molecular weight of 56.10 ± 0.1. No evidence indicating the presence of either high boiling or high molecular weight impurities was obtained.

Spectroscopic tests on this sample gave no evidence for the presence of ethylene. A band at 728 cm^{-1} was observed but not accounted for. In the second sample prepared by the same method this line was not observed so it is almost certainly due to an impurity.

In preparing the second sample fewer precautions were taken to prevent condensation of cyclopentanone in the reaction chamber and as a result some liquid was present during the photolysis. The product obtained was contaminated with butene-1, which was identified spectroscopically by comparison with infra-red ab-

[5] M. Shepherd, Bur. Stand. J. Research **12**, 185 (1934).
[6] Rayleigh, Proc. Roy. Soc. **55**, 340 (1899).

sorption data on this compound very kindly supplied us by the Shell Oil Company, Incorporated, Houston Refinery Research Laboratory.* While their data is only tentative the stronger bands seem fairly definitely established. Bands were observed at 1000 cm^{-1} and 1652 cm^{-1} in our impure cyclobutane (and only in that sample). Both correspond to strong butene-1 bands. After a gas phase bromination of the sample[7] these bands disappeared, and bands at 627, 902, and 1453 cm^{-1} in cyclobutane changed shape, undoubtedly due to removal of the butene-1 which has strong bands at 640, 910, and 1462 cm^{-1} as well as those mentioned above. No bands due to cis- or trans-butene-2,[8] isobutene** or methyl cyclopropane† were observed at any time. Since the bands of butene-1 were observed only in the sample where there was a possibility of liquid phase photolysis, presumably it is a product of that process.

In investigating the presence of butene-1, absorption spectra were taken of the two halves of a distillation of the impure sample from solid CO_2. A distinct difference in the intensities of the lines attributed to butene-1 was observed, as would be expected since butene-1 has about four times the vapor pressure of cyclobutane under these conditions (23.5 mm at $-77.5°C$[9]). Intensities of lines not corresponding to butene-1 remained constant within the error of measurement.

To summarize, then, in the samples whose spectra are reported here there is evidence for the presence of *ca.* $\frac{1}{2}$ percent of ethylene. No other impurities were identified but an infra-red band observed at 728 cm^{-1} is due to an impurity not present in the sample on which the greater part of the infra-red work was done. The same line may appear in the Raman effect since that was studied using the sample first prepared, after the preliminary investigation of the infra-red.

Spectra

The automatic prism spectrometer used in this series of investigations in the infra-red has been described previously.[10] The instrument was calibrated by comparison of known bands of CO_2, C_2H_2, C_2H_4, and CH_3Br with the calculated calibration curve of the prisms used. The CaF_2 prism was used in the range 2 to 8.5μ, the NaCl prism in the range 8 to 14μ, and the KBr prism in the range 13 to 25μ.

The cells used were the 30-cm Pyrex tubes, with KBr windows sealed on the ends with clear Glyptal, which have been used in previous investigations. To prevent attack on the stopcock grease by the hydrocarbon a stopcock with capillary leads was used, and a bead of Hg held in the capillary by the pressure inside the cell kept the gas from coming in contact with the grease.

Figure 1 gives the observed spectrum of cyclobutane. Results of runs in which the sample was contaminated with butene-1 are not included. Everywhere, except for the range above 3200 cm^{-1} the spectrum has been covered more than once, and all bands reported in Table I except those marked with ? were observed in all runs at the higher pressures.

In the spectroscopic investigation of impurities (see above) special attention was paid to the bands at 754 and 737 cm^{-1}. These showed no change in intensity within the limits of error of measurement (about 2 percent on the percent transmission scale) after a distillation which changed the intensity of a comparable line of butene-1 by a factor of 2. Bromination had no effect on their intensity either. If they are due to an impurity its properties must, then, be very similar to those of cyclobutane and we have been unable to find one satisfying the physical requirements which cannot be eliminated on the basis of spectroscopic evidence, or a consideration of the starting material. The bands mentioned have, therefore, been assumed to be actually due to

* Private communication.

[7] By a method similar to that described by A. G. Nickle, Dissertation, Harvard University (1941).

[8] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 247 (1938).

** A search of the literature failed to reveal any infra-red data on this compound, but positions of Raman lines [L. Kahovec and K. W. F. Kohlrausch, Zeits. f. physik. Chemie **46**, 165 (1940)] do not correspond to the observed absorption maxima.

† Since no infra-red data was found in the literature and the Raman spectrum [Lespieau, Bourguel, and Wakeman, Bull. Soc. Chim. Fr. **51**, 400 (1939)] indicated the possibility that lines observed in our material might be due to methyl cyclopropane, some was prepared [N. Demjanoff, Ber. **28**, 21 (1895)] and a tentative absorption spectrum obtained.

[9] C. C. Coffin and O. Maass, J. Am. Chem. Soc. **50**, 1427 (1928).

[10] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 197 (1938) and A. J. Wells, Dissertation, Harvard University (1941). Latter describes changes made since publication of I, including addition of CaF_2 prism.

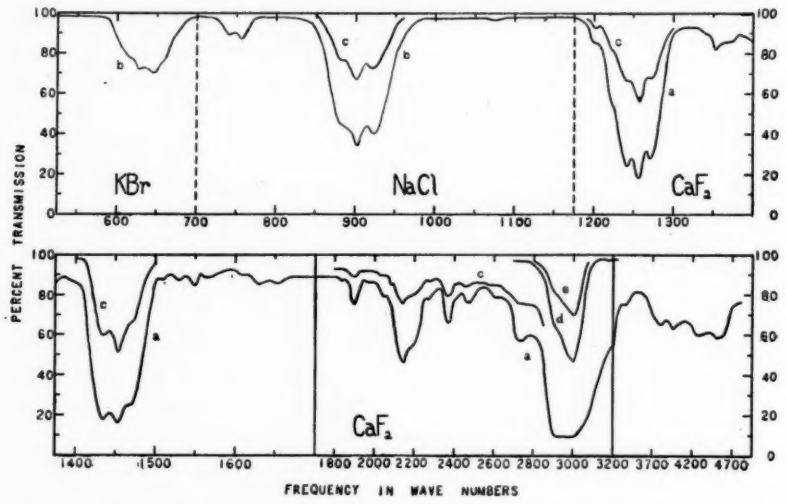

FIG. 1. The infra-red absorption spectrum of cyclobutane. Pressures: (*a*) 165 mm; (*b*) 135 mm; (*c*) 42 mm; (*d*) 3 mm; (*e*) *ca.* 1 mm of Hg.

cyclobutane, which necessitates postulation of an unobserved branch, probably on the low frequency side of the observed pair.

The Raman spectrograph used has also been described[11] previously. Qualitative polarization measurements were made by the "Polaroid" method.[12] The use of dyes and filters to eliminate the Hg green lines and excitation from the 4047 Hg line, which has been described in other papers in this series,[13] proved especially helpful in dealing with this material.

The Raman spectrum of liquid cyclobutane at 25°C was obtained. The small quantity of cyclobutane prepared necessitated the use of a particularly small Raman tube (capacity≦0.5 cc) which is described elsewhere.[14] As shown by the microphotometer traces (Fig. 2) the spectra obtained, while satisfactory in most respects, might not show up very weak shifts since the intensity of the continuous background is rather higher than usual in comparison with that of the light from Raman scattering. The traces also show the difficulty in separating lines. Careful examination of plates and microphotometer traces has led us to the conclusion that the shifts centered around 1450, 1220, and 933 cm^{-1} are probably all doublets, and that the broad band around 3000 cm^{-1} is composed of three lines, but the spacing is so small that exact determination of the positions of the components is impossible. All shifts reported may be out by at least ± 5 cm^{-1}.

The very weak line reported at 750 cm^{-1} was observed on two plates though its intensity was so low that its separation from the background was not definite on the microphotometer traces. It cannot be regarded, then, as any more than probable, and if it is present we believe it to be due to an impurity. This would correspond to the 728 cm^{-1} band observed in the infra-red spectrum of the sample of cyclobutane used for the Raman work (see section on purity of product).

Table I gives the frequencies of the absorption maxima observed in the infra-red spectrum and their relative intensities, together with the probable band type (perpendicular or parallel) and an assignment of "*P*," "*Q*," and "*R*" branches in cases where these could be determined (see assignment). The table also includes shifts observed in the Raman effect, the exciting lines from which these shifts were observed, relative intensities, and an indication of whether or not they appear polarized.

[11] H. Gershinowitz and E. B. Wilson, Jr., J. Chem. Phys. **6**, 247 (1938).
[12] J. T. Edsall and E. B. Wilson, Jr., J. Chem. Phys. **6**, 124 (1938).
[13] Cf. A. J. Wells and E. B. Wilson, Jr., J. Chem. Phys. **9**, 314 (1941).
[14] H. D. Noether, Dissertation, Harvard University (1942).

THEORETICAL

Symmetry of Cyclobutane

Recent calculations by Aston et al[15] on the configuration of cyclopentane have presented the possibility that the ring in that substance is deformed in such a way that one of the carbon atoms is out of the plane of the other four. If so, then one might be justified in considering a non-planar structure of the ring in cyclobutane as well.

The symmetry of cyclobutane if the ring is distorted out of a plane is that of the point group C_{2v}, whereas if the ring is planar the symmetry is D_{4h}. If it is the latter a center of symmetry is present and in such a case the selection rules forbid the appearance of frequencies corresponding to the same vibration in both the Raman and infra-red spectra. If, on the other hand, the symmetry is C_{2v}, all vibrations active in one may also appear in the other. In the observed spectra some approximate coincidences do occur (at 3000, 1450, 1240 and possibly 900 cm^{-1}) but all these can be explained as readily on the basis of the D_{4h} as on the C_{2v} selection rules. Accidental coincidences due to similarity, but not identity, of types of molecular vibrations are expected, and bands at the frequencies mentioned occur in most hydrocarbons. The points of greater interest are the cases where lines occurring in one spectrum do not appear in the other. The band in the infra-red spectrum at 627 cm^{-1} has apparently no analogue in the Raman spectrum and the line at 1010 cm^{-1} in the latter almost certainly does not appear in the former. Since the latter line is highly polarized it is probably the symmetrical "breathing" frequency of the ring (see assignment) and this should appear in the infra-red spectrum if not forbidden by selection rules.

Besides the lack of coincidence in the two spectra we may point out the small number of bands appearing in the infra-red. Only four strong bands are observed in the range 400–1500 cm^{-1}, in agreement with predictions from the D_{4h} selection rules, but definitely not in agreement with those of C_{2v} which would permit the appearance of sixteen bands. The same argument disposes of the possibility that the symmetry is V_h (distortion of the ring in the plane), in which case eight fundamentals should appear. Since fundamentals permitted by the selection rules to appear in the infra-red usually do so, the conclusion seems obvious.

Table II gives selection rules and polarization

TABLE I.

Infra-red			Raman	
Frequency (cm^{-1})		Intensity and type[a]	Shift* (cm^{-1})	Intensity and[a] polarization
4500		4		
4250		4		
3950		3		
3775		3		
3350		1		
3190		1		
			2988	8
2990		20	2962 (*e*, *k*)	12
2900		8	2938	8 (*P*)
2735		4		
2626		1	2880 (*e*, *k*)	3 (*P*)
2463		2		
2360		3		
2272		0		
2183		4		
2145		5		
2090?		0		
2050		1		
1987?		0		
1896		2		
1827		0		
1653	*R*?	1		
1636	*Q*?			
1607?	*P*?	0		
1565	*R*?			
1547	*Q*?	1		
1528	*P*?			
1511?		0		
1466	*R*		1465 (*e*, *k*)	4 (*P*)
1453	*Q*	10 (⊥)	1445 (*e*, *k*)	4
1436	*P*			
1371	*R*			
1355	*Q*	2 (⊥?)		
~1340	*P*			
1272	*R*			
1257	*Q*	10(⊥)		
1243	*P*			
1216			1228 (*e*)	2
1200		1	1209 (*e*)	3 (?)
1070?		0	~1110? (*e*)?	0
925	*R*		1010 (*e*, *f*, *k*)	10 (*P*)
902	*Q*	8 (‖)		
885	*P*			
			933 (940?) (923?) (*e*, *k*)	7*b*
754		2	~ 750? (*e*)?	0 (*P*?)
737				
644	*R*			
627	*Q*	5 (⊥)		
617	*P*			

[a] See text for differentiation between types of bands.
* The letters in parentheses following the frequencies of the Raman shifts indicate the exciting lines from which these shifts were observed. Kohlrausch's nomenclature is employed.

[15] J. G. Aston, S. C. Schumann, H. L. Fink, and P. M. Doty, J. Am. Chem. Soc. **63**, 2029 (1941).

or band types of the active vibrations of cyclobutane if the symmetry is D_{4h}.[15a]

Assignment of Frequencies

A description of the types of vibrations occurring in the various representations is given in Table III. We are using the nomenclature developed by Linnett[16] to differentiate between the various possible motions of the methylene group, except that the motion he referred to a bending

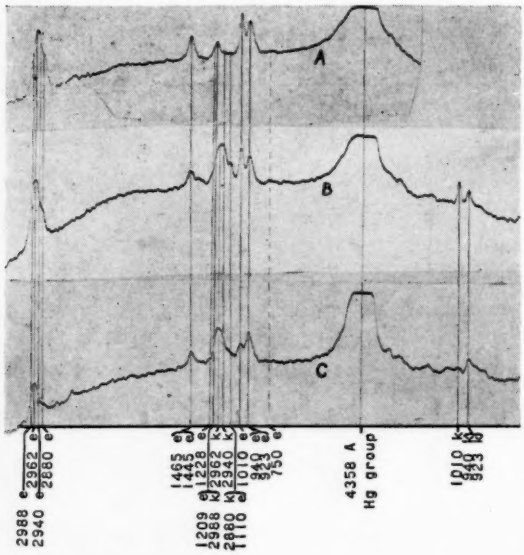

FIG. 2. Microphotometer traces of Raman spectra of cyclobutane. All plates taken with 0.09 g/l. Rhodamine 5 *GDN* extra in the alcohol circulated in the cooling system. Filters used besides this were: (*A*) Wratten No. 2*A* around the Raman tube; (*B*) no other filters; (*C*) Polaroid around the Raman tube to polarize incident light parallel to the axis of the tube.

we prefer to call wagging both to prevent confusion with the so-called bending motions of the CH_3 group which are more closely related to the "CH_2 deformation" and because we feel the latter term to be somewhat more descriptive. This system we have found quite convenient both in discussions and in calculations.

Starting with the simplest and perhaps most definite case, we may assign frequencies to the A' vibrations on the basis of the Raman polarization. It will be seen from Table I that only four lines show definite polarization. The 2940 and 2880 cm^{-1} lines are clearly the symmetrical C−H stretching and 2×1450 resonating with it. 1465 cm^{-1} is the CH_2 deformation and 1010 cm^{-1} the symmetrical "breathing" frequency of the ring by obvious frequency arguments. The latter is close to a prediction by Aubert[17] but does not check too well with what Kohlrausch and Skrabal[18] expected from work on derivatives.

The other representations on which we have sufficient evidence to make a definite assignment are the infra-red active A_2'' and E''. In cyclobutane it is easily possible to differentiate between vibrations with these symmetries by the band envelopes. Calculations from the moment of inertia of the molecule using Gerhard and Dennison's[19] formula for the $P-R$ spacing of parallel bands in symmetrical top molecules lead us to expect this spacing to be 39 cm^{-1} for A_2'' bands. We observe spacings of 40 cm^{-1} in the 902 cm^{-1} band, and 30, 29, and 27 cm^{-1}, respectively, in the 1453, 1257, and 627 bands. Eliminating 737 cm^{-1} as a possible fundamental (this will be considered later), it is obvious that 902 cm^{-1} is the A_2'' rocking* and the other three are the E'' fundamentals. The normal coordinate treatment in E'' shows that 1453 cm^{-1} is principally CH_2 deformation, 1257 cm^{-1} CH_2 wagging, and 627 cm^{-1} the degenerate ring deformation. The low frequency of the ring deformation we believe to be primarily due to the large interaction between the C−C stretching and the C−C−C angle bending (see Table V). The C−H stretchings are uncertain but surely near 2990 cm^{-1} in both A_2'' and E''. The values given in Table III for these motions are guesses.

The other directly observed frequencies are the depolarized Raman shifts. Of these, that at 1445 cm^{-1} must be the B_2' CH_2 deformation since it is the only line left near the expected frequency. In accordance with Kohlrausch's[18] predictions, and because the line is the strongest in the proper frequency range, we assign the 940 cm^{-1} shift to the unsymmetrical ring stretching in B_1'. The unpolarized CH stretches at 2988 and 2962 are

[15a] J. E. Rosenthal and G. M. Murphy, Rev. Mod. Phys. **8**, 317 (1936).
[16] J. W. Linnett, J. Chem. Phys. **6**, 695 (1938).
[17] M. Aubert, Comptes rendus **203**, 661 (1936).
[18] K. W. F. Kohlrausch and R. Skrabal, Zeits. f. Electrochemie **43**, 282 (1937); or K. W. F. Kohlrausch, *Der Smekal-Raman effect*, Erganzungsband (Springer, Berlin).
[19] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).
* See also Table III for an *a priori* calculation of A_2'' frequency.

assigned as indicated in Table III because the form of the force constants in the Raman active representations leads us to expect the E' frequency to have a value between those in A_1' and B_2'.

The remaining lines observed are not so readily or definitely assignable. To distinguish between them we have resorted to the results of the normal coordinate treatment. Using Stitt's value[20] for the C−C−H bending constant, H_β, and a value of the C−C−C bending constant estimated from Wilson and Wells' work[21] on propylene we have come to the conclusion that the frequencies observed at 1228 cm^{-1}, 1209 cm^{-1}, and 923 cm^{-1} are probably to be assigned as indicated in Table III. These calculations also lead to a prediction of about 600 cm^{-1} for the B_2' in-plane ring bending. A careful examination of this region on the Raman plates has failed to reveal any line below 750 cm^{-1}. Since an alternative explanation of the 750 cm^{-1} line is available (see under Spectra) and since it is definitely higher than the value we expect for the fundamental, we are of the opinion that the shift corresponding to the fundamental was not observed.

TABLE II.

Representation	Symmetry with respect to I	C_4	$2\sigma_v$*	Number of fundamentals	Selection† rules
A_1'	S	S	S	3	R (P)
A_2'	S	S	A	1	F
B_1'	S	A	A	2	R (dp)
B_2'	S	A	S	3	R (dp)
E'	S	degenerate		3	R (dp)
A_1''	A	S	A	1	F
A_2''	A	S	S	2	I–R ($\parallel$)
B_1''	A	A	S	3	F
B_2''	A	A	A	1	F
E''	A	degenerate		4	I–R ($\perp$)

* Planes $\perp$ plane of the ring and bisecting the C−C−C angles.
† R = Raman active, I–R = infra-red active, F = inactive in both spectra, P = polarized, dp = depolarized, $\parallel$ = parallel type band, $\perp$ = perpendicular type band.

The doubtful Raman line at 1110 cm^{-1}, if present, we believe to be one of the non-degenerate CH_2 twisting frequencies. The appearance of either would violate the D_{4h} selection rules, but such a violation might occur in the liquid phase spectrum. The appearance of fairly strong lines at very nearly this frequency in all cyclobutane derivatives investigated by Kohlrausch, Reitz, and Skrabal[18,22] (except cyclobutanone where the strain introduced by the carbonyl group may account for its absence) serves to confirm our hypothesis. We have assigned it to A_1'' on the basis of calculations from the constants used in E'.

TABLE III.

Representation	Type of vibration*	Frequency Assigned*	Frequency Calculated
A_1'	C−H stretching	2940, 2880 cm^{-1}	—
	CH_2 deformation	1465	1467 cm^{-1}
	ring stretching	1010	1011
A_2'	CH_2 wagging	1260	1260
B_1'	CH_2 wagging	1228	1229
	ring stretching	940	938
B_2'	C−H stretching	2988	—
	CH_2 deformation	1445	1441
	ring bending (in plane)	595	597
E'	C−H stretching	2962	—
	CH_2 twisting	1209	1207
	CH_2 rocking	923	918
A''	CH_2 twisting	1110	1058
A_2''	C−H stretching	2980	—
	CH_2 rocking	902	886
B_1''	C−H stretching	2985	—
	CH_2 rocking	1200	1225
	ring bending (out of plane)	145	—
B_2''	CH_2 twisting	1058	1058
E''	C−H stretching	2990	—
	CH_2 deformation	1453	1500
	CH_2 wagging	1257	1291
	ring deformation	627	624

* See text.

The fundamentals not observed we have assigned from consideration of the combination bands appearing in the infra-red spectrum, together with calculations using Stitt's H_β[20] and consideration of the spectrum of derivatives.[18,22] The two ring bending motions, in and out of the plane, were assigned on the basis of the two lowest definite combination bands appearing in the infra-red. The 737 cm^{-1} band is believed to be a combination since it may reasonably be explained as such as indicated in Table IV, whereas 627 cm^{-1} could not be. Also, its intensity is probably low for a fundamental but high for a difference "tone," the other possible source of such a band if impurities are excluded. Unfortunately this band is so weak that we have been

[20] F. Stitt, J. Chem. Phys. **7**, 297 (1939).
[21] E. B. Wilson, Jr., and A. J. Wells, J. Chem. Phys. **9**, 319 (1941).
[22] K. W. F. Kohlrausch and R. Skrabal, Monats. f. Chem. **70**, 44 (1937); O. Reitz and R. Skrabal, Monats. f. Chem. **70**, 398 (1937); R. Skrabal, Monats. f. Chem. **70**, 460 (1937).

unable to determine its envelope, which would confirm or disprove the assignment in Table IV.

It will be noted that the assignment of fundamentals given in Table III offers an explanation of all bands observed with the exception of the doubtful one at 1511 cm^{-1}. That is very weak and in the region of strong absorption by atmospheric water so its presence is distinctly uncertain.

Calculations

In all calculations on cyclobutane we have assumed, in the absence of experimental evidence, that it has the following dimensions:

$$C-C=1.53A,^{23}$$
$$C-H=1.09A,^{24}$$
$$C-C-C \text{ angle}=90°,$$
$$H-C-H \text{ angle}=109°\ 28' \text{ (tetrahedral)},$$
$$C-C-H \text{ angle}=114°\ 6'.$$

Another plausible assumption would have been to take the C−C−H and H−C−H angles equal (112° 59′). The difference is negligible for our purposes. With the same force constants, frequencies are different by less than 2 percent when calculated on the two assumptions.

The secular equation was set up in valence type symmetry coordinates[25,26] and the results were checked by repeating the process using a different method recently developed by C. W. Lippman.[27] We would like to take this opportunity to thank the latter for giving us the details of his method prior to its publication. C−H stretches were factored out[25] and treated separately. The treatment showed Stitt's K_H[20] to be a satisfactory force constant for this molecule.

The internal coordinates selected for treatment of this problem were the sets of changes in the four C−C distances, the eight C−H distances, the four H−C−H angles, the sixteen C−C−H angles and the four C−C−C angles. The symbols used here to represent these changes are, respectively, R_i, r_i, α_i, β_i, and γ_i. In Fig. 3 are shown some of the coordinates around a single carbon atom to illustrate the system of numbering coordinates. Subscripts on α's and γ's, not shown, are the numbers of the central carbon atom of the corresponding angles.

The out of plane bending of the ring was not treated and another type of coordinate would have to be added to include it. Omission of this motion does not necessarily imply that the B_1'' representation, in which it occurs, cannot be treated since it is such a low frequency that

TABLE IV.*

Observed frequency	Assignment	Symmetry
737 cm^{-1}	145+ 595= 740[a]	A_2''
~1070?	145+ 923=1068	E''
1216	595+ 627=1222[a]	E''
1355	145+1209=1354	E''
1511?	?	
1547	627+ 923=1550	A_2''
1565	627+ 940=1567	E''
1607?	145+1445=1590	A_2''
1636	627+1010=1637	E''
1827	902+ 923=1825	E''
	627+1209=1836	A_2''
1896	902+1010=1912	A_2''
	627+1260=1887	E''
1987?	940+1050=1990	A_2''
2050	595+1453=2048	E''
~2090?	627+1465=2092	E''
2145, 2183	Σ900+1200	A_2'', E''
2272	1050+1230=2280	A_2''
2360	1110+1260=2370	A_2''
	902+1465=2367	A_2''
	923+1453=2376	E''
2463	1010+1453=2463	E''
	1209+1257=2466	A_2''
2626	1200+1445=2645	A_2''
2735	1257+1465=2722	E''
	1260+1453=2713	
2880 (*R*)	2×1450=2900	A_1'
2900	1453+1465=2918	E''
	1445+1453=2898	
3190	1010+Σ900+1200 (see above)	A_2'', E''
3350	1010+2360 (see above)	A_2'', E''
3775	3×1257=3771	A_2'', E''
	other combinations of three 1200 ν's	
	1010+1257+1465=3732, etc.	
3950	1010+2980=3990	A_2'', E''
	940+2990=3930, etc.	
4250	Σ3000+1200	A_2'', E''
4500	Σ3000+1450	A_2'', E''

* This table certainly does not include all combinations which might explain the observed lines. Except in a few cases where it was necessary, combinations of three fundamentals are not used to explain lines. These undoubtedly could be observed in a case such as this where the frequencies occur in groups.

[a] See text.

(*R*) Observed in the Raman spectrum.

[23] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. **59**, 1223 (1937).

[24] N. Ginsburg and E. F. Barker, J. Chem. Phys. **3**, 668 (1935).

[25] E. B. Wilson, Jr., J. Chem. Phys. (a) **7**, 1047 (1939); (b) **9**, 76 (1941).

[26] M. A. El'yashevich, J. Phys. Chem. U.S.S.R. (a) **14**, 1381 (1940); (b) **15**, 831 (1941).

[27] C. W. Lippman, soon to be published.

interactions with other vibrations in the representation are probably negligible. If so, it may be factored out by setting the corresponding force constant equal to zero.

The four types of motions of the CH_2 group (see above) may be represented in terms of β's (for carbon atom C_1) as:

$$\begin{aligned} CH_2 \text{ deformation} &= \beta_1+\beta_2+\beta_3+\beta_4 = d_1{}^*, \\ CH_2 \text{ wagging} &= \beta_1+\beta_2-\beta_3-\beta_4 = w_1, \\ CH_2 \text{ twisting} &= \beta_1-\beta_2+\beta_3-\beta_4 = t_1, \\ CH_2 \text{ rocking} &= \beta_1-\beta_2-\beta_3+\beta_4 = v_1. \end{aligned}$$

Analogous combinations represent the same motions on other carbon atoms.

The redundancy conditions on the coordinates used are:

(1) At each carbon atom:
$2\sqrt{2}\alpha_i+\sqrt{5}(\beta_1+\beta_2+\beta_3+\beta_4)_i+2\gamma_i=0$;
(2) $\gamma_1+\gamma_2+\gamma_3+\gamma_4=0$;
(3) $2(R_1-R_3)+R_0(\gamma_1+\gamma_2-\gamma_3-\gamma_4)=0$;
(4) $2(R_2-R_4)-R_0(\gamma_1-\gamma_2-\gamma_3+\gamma_4)=0$.

A complete treatment of the vibrational problem has proved possible assuming Stitt's[20] constant H_β for the C−C−H angle change. As shown in Table III the maximum deviation, +3.2 percent of calculated from definitely observed frequencies, occurs in E'', where the number of interactions possible but neglected is larger than in the other cases. The fit could be improved by adjusting some of these, but in view of the uncertainties both in the actual value of the C−C−H angle constant and in the geometry of the model, it was felt that this would only add to the complexity of the potential function without necessarily improving it. The C−C−H angle constant has not been evaluated from the data observed here since a number of interactions between these coordinates appear to be of some importance. On the average, Stitt's value appears to be as satisfactory as possible without including these interactions.

The force constants used in the potential function are given in Table V. The constants given are for internal coordinates except for F_d and $F_{\beta\beta}(E')$. The former is the constant for the combination of changes in the angles around one carbon giving rise to the "CH_2 deformation" when the corresponding element in the G matrix[25] is obtained from α only. Due to the redundancy,

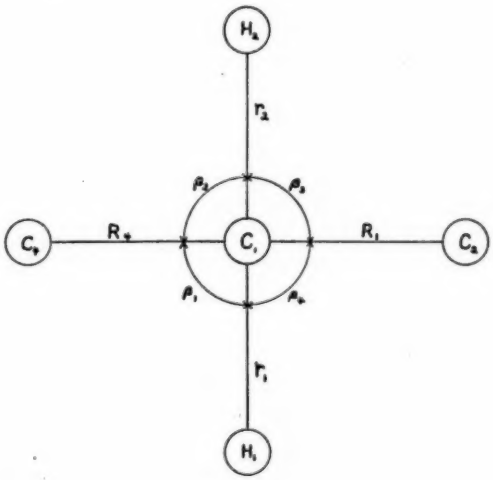

FIG. 3. Here the actual bonds and angles are labeled R, r, etc. In the text it is the corresponding changes to which these symbols refer.

f_α always appears in this combination. If we assume Stitt's H_β[20] to be transferable, F_d may be broken down, leading to a value of $f_{\alpha\beta}=0.047$. This is approximately four times the value Stitt found in ethane, but still possible. If, however, we assume $f_{\alpha\beta}=0$ then $f_\alpha=0.428$ (cf. 0.547 from Stitt's H_α) which is an unexpectedly large change. The truth may well lie somewhere between these two.

$F_{\beta\beta}(E')$ is the interaction appearing in the E' representation between the two combinations of β's appearing there. This is the only interaction between angles which we can be nearly certain is present, although in view of the uncertainty in f_β, its numerical value is not definite.

Discussion of Force Constants

The only force constant evaluated which shows definitely a change from that obtained in unstrained cases is f_R. This is reduced about 5 percent from the value obtained by Stitt[20] in his work on ethane, and about 8 percent from the

* The "CH_2 deformation" as described by Linnett, reference 16, requires a change in the α as well as the β's on the carbon atom. Actually these coordinates and the corresponding γ are involved in a redundancy relation and so are not independent.

TABLE V.

Constant*	Value	Coordinates involved
f_R	$4.26\times10^{5}\ \frac{\text{dynes}}{\text{cm}}$	R_i
$f_{R\alpha}$	$-0.059\times10^{-3}\ \frac{\text{dyne}}{\text{radian}}$	the type $R_1\alpha_1$
$f_{R\beta}$	$0.108\times10^{-3}\ \frac{\text{dyne}}{\text{radian}}$	the type $R_1\beta_3$
$f_{R\gamma}-f'_{R\gamma}$	$1.19\ \times10^{-3}\ \frac{\text{dyne}}{\text{radian}}$	the types $R_1\gamma_1$, $R_1\gamma_3$†
F_d**	$0.690\times10^{-11}\ \frac{\text{dyne-cm}}{\text{radian}^2}$	$\alpha(\Gamma_i)$[a]
f_β (reference 20)	$0.654\times10^{-11}\ \frac{\text{dyne-cm}}{\text{radian}^2}$	β_i
f_γ	$0.767\times10^{-11}\ \frac{\text{dyne-cm}}{\text{radian}^2}$	γ_i
$F_{\beta\beta}(E')$	$-0.023\times10^{21}\ \frac{\text{dynes}}{\text{cm}^3\,\text{radian}^2}$	$\beta'(E')\beta''(E')$‡

* The interaction constants given here are taken from matrix expressions for the potential energy. For use in the quadratic form of this quantity they should be multiplied by 2.

** $F_d=f_\alpha-4(2/5)^{\frac{1}{2}}f_{\alpha\beta}+(2/5)f_\beta$.

[a] See text.

† In that order.

‡ In both degenerate representations there are, of course, two equivalent, orthogonal sets of coordinates, of which only one was considered in the calculations. In each set two combinations of β's appear as symmetry coordinates. These have been denoted by the superscripts $'$ and $''$. In E' the two β coordinates in the set used are

$$\beta'(E') = \tfrac{1}{4}R_0r_0(t_1+t_2-t_3-t_4),$$
$$\beta''(E') = \tfrac{1}{4}R_0r_0(v_1-v_2-v_3+v_4),$$

in the notation given in the text.

value predicted for a C−C bond length of 1.53A by Crawford and Brinkley's[28] relation. This is in qualitative agreement with results of Kohlrausch and co-workers.[29]

We have found no suitable constant with which to compare f_γ so determination of the effect of strain on this will have to wait until one is evaluated. Since the corresponding angle is considerably strained we might expect an appreciable effect.

Two other interesting features of the potential function obtained, presumably effects of the strained configuration, are the absence of interactions between C−C stretches and the large interaction between R and γ. Also, the agreement between F_{Rd}* and Stitt's $K_{C\gamma}$, analogous constants corresponding to the interaction between R and a symmetrical deformation of the angles around the carbons which it connects, is rather striking. Unfortunately, until further evidence is available on hydrocarbons, both cyclic and noncyclic, it appears useless to try to develop general theories on their potential functions.

I should like to take this opportunity to express my thanks to Professor E. B. Wilson, Jr., both for suggesting this problem to me and for his continued interest and many helpful suggestions throughout the course of the work.

[28] B. L. Crawford and S. R. Brinkley, Jr., J. Chem. Phys. **9**, 69 (1941).

[29] Kohlrausch and Seka, Ber. **69**, 729 (1936); Kohlrausch and Skrabal, Monats. f. Chem. **70**, 44 (1937).

* Interaction between the CH_2 deformation and the C−C stretching symmetry coordinates.

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Some Remarks on the Kinetics of Vinyl Derivative Polymerization

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The various elementary steps of vinyl polymerization reactions are discussed. Activation is considered to occur by collision of an unactivated monomer either with another monomer, a catalyst, a solvent, or a polymer molecule. It is further taken into account that certain types of active nuclei can be more easily deactivated than others. Two steps of propagation are considered: normal chain growth and chain transfer. Termination of growing chains is assumed to be possible either by collision with another growing chain, with an activated monomer, with a molecule of the catalyst, or with certain chain breaking impurities. Using the assumption that for a certain period of the reaction a steady state of activated centers is maintained, equations are derived for the initial over-all rate of the reaction and for the number average polymerization degree. These equations are compared with experiments which have been carried out on the polymerization of styrene at various temperatures, monomer concentrations, and catalyst concentrations. Comparison between theory and experiments shows that in first approximation, the initial over-all rate of the reaction and the initial number average polymerization degree can be represented by the derived equations.

I. INTRODUCTION

IN the last few years a number of experimental studies on the kinetics of vinyl-type polymerization have been published, investigating the rate of these processes as functions of various experimental parameters, such as chemical nature, concentration (or better activity) or partial pressure of monomers, temperature, chemical character and amount of catalyst, nature of solvents, etc.[1]

The monomers used were mainly styrene, vinyl acetate, vinyl chloride, and acrylic acid derivatives, the catalysts peroxides, ozonides, free radicals or metal halides, the solvents hydrocarbons, ketones, substituted phenols, and chlorinated hydrocarbons. The temperature range was between 60° and 150°C.[2]

The results of these investigations provide a very useful background for developing a quantitative scheme for such composite processes. All investigators agree that they involve a number of characteristic individual steps, such as *activation* and *deactivation* of the monomer, *propagation* of the activated monomer into long chains with an activated end (or two activated ends), *transfer* of the activation to another molecule (monomer or solvent), *branching* of the growing chains and termination of the growth in various ways.[3] The first task for a numerical treatment of such composite reactions is always to find out how the different elementary steps cooperate in producing and consuming various intermediate (short-living) configurations and how they finally build up the stable end-product with its characteristic properties, such as average polymerization degree, molecular size distribution, frequency of branching, etc. In practically all of the papers quoted above, the authors have carried out an analysis of this kind and in most cases succeeded in deriving formulas which closely agreed with their experimental findings.

[1] R. E. Burk, H. E. Thompson, A. J. Weith, and I. Williams, *Polymerization* (Reinhold Publishing Company, New York, 1937); H. Mark and R. Raff, *High Polymeric Reactions* (Interscience Publishers, New York, 1941).

[2] J. Abere, G. Goldfinger, H. Mark, and H. Naidus, Paper presented at the Buffalo Meeting of the American Chemical Society in September, 1942; H. N. Alyea, J. J. Gartland, and H. R. Graham, Ind. Eng. Chem. **34**, 458 (1942); H. Dostal, H. Mark, and R. Raff, Ind. Eng. Chem. **29**, 595 (1937); A. C. Cuthberson, G. Gee, and E. K. Rideal, Nature **140**, 889 (1937); C. S. Marvel and J. C. Cowan, J. Am. Chem. Soc. **61**, 3156 (1939); C. S. Marvel, J. Dee, and H. G. Cooke, J. Am. Chem. Soc. **62**, 3499 (1940); C. S. Marvel, G. D. Jones, T. W. Mastin, and G. L. Schertz, J. Am. Chem. Soc. **64**, 2356 (1942); H. W. Melville, Proc. Roy. Soc. **A165**, 163, 511 (1937); **A167**, 99 (1938); J. K. Moore, R. E. Burk, and H. P. Lankelma, J. Am. Chem. Soc. **63**, 2954 (1941); R. G. W. Norrish and E. F. Brockman, Proc. Roy. Soc. **A163**, 205, (1937); **A171**, 147 (1939); Trans. Faraday Soc. **35**, 1087 (1939); R. G. W. Norrish and R. R. Smith, Nature **150**, 336 (1942); H. Pfann, Thesis, Brooklyn Polytechnic Institute (May, 1942); C. C. Price and R. W. Kell, J. Am. Chem. Soc. **63**, 2798 (1941); C. C. Price, R. W. Kell, and E. Krebs, J. Am. Chem. Soc. **64**, 1103 (1942); C. C. Price and D. A. Durham, J. Am. Chem. Soc. **64**, 2508 (1942); G. V. Schulz, H. Dinglinger, and E. Husemann, Zeits. f. physik. Chemie **B34**, 187 (1936); **B36**, 184 (1937); **B39**, 246 (1938); **B43**, 385 (1939); **B50**, 305 (1941); Naturwiss. **27**, 387, 659 (1939); H. Staudinger and G. V. Schulz, Ber. **68**, 2320 (1935).

[3] P. J. Flory, J. Am. Chem. Soc. **59**, 241 (1937); R. Ginell and R. Simha, J. Am. Chem. Soc. **65**, 706, 715 (1943); H. Mark and R. Raff, *High Polymeric Reactions* (Interscience Publishers, Inc., New York, 1941); New York Acad. Sci., Discussion on High Polymers (January, 1943).

As necessary, however, in pioneering work of this kind, emphasis was mainly laid on the special case under consideration and the experimental parameters listed above were not always varied over as wide a range as would be desirable for a systematic study of these processes. It was therefore felt that it might be appropriate to help extend our present knowledge by a *more systematic* study of a few particularly interesting systems. Two monomers (styrene and methacrylic ester) were selected and their polymerization was (and is still being) studied in several typical solvents (methyl ethyl ketone, carbon tetrachloride, toluene, benzene) over a fairly wide range of catalyst concentration using different types of catalysts (benzoylperoxide, *p*-Br-benzoylperoxide, tin tetrachloride), various initial monomer concentrations (10–80 percent), various types and activities of inhibitors, and working at temperatures between 60 and 150°C. Some of the results have been presented previously and are being published in more detail elsewhere.[4] In order to evaluate and coordinate them it seemed useful also to extend somewhat the formal kinetic scheme for such processes. This is the purpose of the present paper.

It must be emphasized, however, that formal kinetics is not the final goal of the quantitative study of a polymerization reaction. What we would like to arrive at is a full understanding of the *chemical nature* of each single elementary step such as activation, propagation, termination, etc. To reach this goal, however, it seems necessary first to describe each of these steps quantitatively and, if possible, to assign to each of them a certain *order of reaction*, a definite *frequency factor* and a specific *activation energy*. Such numerical characterization is very helpful in narrowing down the speculations as to the chemical nature of these individual elementary processes, and eventually allows the interpretation of them as a certain change in the electronic structure of the molecules involved (opening and closing of covalent bonds, polarization of the double bond, displacement of a pair of electrons, etc.).

[4] J. Abere, G. Goldfinger, H. Mark, and H. Naidus, Paper presented at the Buffalo Meeting of the American Chemical Society in September, 1942; New York Academy of Science, Discussion on High Polymers, January 8 and 9, 1943.

Systematic formal treatments of polyreactions have been carried out previously by Breitenbach,[5] Flory,[6] Raff,[7] and Schulz[8] and the general aspect of vinyl polymerization has been qualitatively correlated with the fundamental properties of the aliphatic double bond. This correlation has been very definitely improved and extended to other characteristic properties of the double bond (cis-trans-isomerization, addition reaction) by the recent work of Eyring and his collaborators.[9]

In all the following calculations, we shall use the Bodenstein principle, assuming that after a comparatively short time a steady state of active (growing) centers is established and maintained throughout a considerable period of the experiment. This simplifying assumption has been always used, and is presumably in most cases (moderate amount of polymer being formed, presence of solvents) good enough for the interpretation of the experiments. It must, however, be kept in mind that it represents an oversimplification of the actual conditions, and it is of importance that Ginell and Simha[3] have recently carried through the integration of the general differential equations of a polymerization reaction without any restricting assumption of this kind. Their results are of great value to decide whether under given conditions the Bodenstein principle can be legitimately applied or not.

II. DISCUSSION OF THE ELEMENTARY REACTIONS

Let us first consider the *activation* or *nucleus formation*. It is not yet definitely established whether pure thermal activation can take place

[5] J. W. Breitenbach and R. Raff, Monats. f. Chem. **69**, 1107 (1936); J. W. Breitenbach and H. Rudorfer, Monats. f. Chem. **70**, 37 (1937); J. W. Breitenbach, Monats. f. Chem. **71**, 275 (1938); J. W. Breitenbach and H. Maschin, Zeits. f. physik. Chemie **A187**, 175 (1940).

[6] P. J. Flory, J. Am. Chem. Soc. **59**, 241 (1937); **62**, 1057, 1561, 2255 (1940).

[7] H. Dostal, H. Mark, and R. Raff, Ind. Eng. Chem. **29**, 595 (1937); H. Mark and R. Raff, *High Polymeric Reactions* (Interscience Publishers, New York, 1941).

[8] G. V. Schulz, H. Dinglinger, and E. Husemann, Zeits. f. physik. Chemie **B34**, 187 (1936); **B36**, 184 (1937); **B39**, 246 (1938); **B43**, 385 (1939); **B50**, 305 (1941); Naturwiss. **27**, 387, 659 (1939); H. Staudinger and G. V. Schulz, Ber. **68**, 2320 (1935).

[9] R. A. Harman and H. Eyring, J. Chem. Phys. **10**, 557 (1942); J. L. Magee, W. Shand, and H. Eyring, J. Am. Chem. Soc. **63**, 677 (1941); R. G. W. Norrish and R. R. Smith, Nature **150**, 336 (1942); T. Ri and H. Eyring, J. Chem. Phys. **8**, 433 (1940).

by the collision of two monomers, but the course of the polymerization of ethylene and styrene at high temperatures in the gaseous phase seems to indicate its existence. The possible results of such a step are:*

$$CH_2=CH_2+CH_2=CH_2\rightarrow CH_2=CH_2+-CH_2-CH_2-, \quad (1)$$

$$CH_2=CH_2+CH_2=CH_2\rightarrow -CH_2-CH_2-CH_2-CH_2-, \quad (2)$$

$$CH_2=CH_2+CH_2=CH_2\rightarrow -CH_2-CH_2-+-CH_2-CH_2-, \quad (3) \quad (1u)$$

$$CH_2=CH_2+CH_2=CH_2\rightarrow -CH_2-CH_3+-CH=CH_2, \quad (4)$$

$$CH_2=CH_2+CH_2=CH_2\rightarrow CH_3-CH_3+-CH=CH-. \quad (5)$$

Cases (1*u*, 1) to (1*u*, 3) represent only exchange of energy between the colliding particles, while (1*u*, 4) involves the exchange of *one* hydrogen atom and (1*u*, 5) the exchange of even *two* of them. The activation energy for these two cases is presumably rather high[10] and they will be infrequent at temperatures below 200°C. The third reaction involves also a high activation energy and—even if it occurred—will presumably have the tendency to go over into (1*u*, 2). Hence, we shall only include (1*u*, 1) and (1*u*, 2) in the further discussion. In the following we shall always denote the monomer with m_1, the dimer with m_2, etc.; activation on one or both ends of the chain is indicated by an asterisk. The two above cases can therefore be written as

$$m_1+m_1\rightarrow m_1+{}^*m_1{}^*, \quad (1u, 1)$$
$$m_1+m_1\rightarrow {}^*m_2{}^*. \quad (1u, 2)$$

Their nature as activation processes is indicated by the fact that there are no asterisks on the left-hand sides, but there are some on the right-hand sides of the equations; activation is *produced*.

Another process of nucleus formation is the collision of m_1 with a catalyst c, which take places as

$$m_1+c^*\rightarrow cm_1{}^* \quad (1),$$
$$\text{or as} \quad m_1+c\rightarrow {}^*m_1{}^*+c \quad (2), \quad (1c)$$
$$\text{and} \quad m_1+cc\rightarrow cm_1{}^*+c^* \quad (3).$$

(1*c*, 1) or (1*c*, 3) seem to be characteristic for peroxide and radical type catalysts, while (1*c*, 2) appears to represent the action of metal-halide catalysts such as BF_3,[11] $AlCl_3$, and $SnCl_4$.[12]†

Collision with a solvent molecule has also been observed to produce nucleus formation, if the energy involved is sufficient. Again we have to consider two typical cases:

The solvent molecule splits into radicals $m_1+ss_1\rightarrow sm_1{}^*+s_1{}^*$. (1) (1*s*)

The solvent polarizes the monomer and facilitates opening of the double bond $m_1+s\rightarrow {}^*m_1{}^*+s$. (2)

Finally we want to include activation by a vigorous collision with a terminated polymer m_j, which might play a role in the later stages of the reaction, when much polymer is formed and which we can write as

$$m_1+m_j\rightarrow {}^*m_1{}^*+m_j. \quad (1p)$$

Altogether, we can summarize the different activation processes as follows:

$$m_1+m_1\rightarrow {}^*m_1{}^*+m_1, \quad (1u, 1)^{**}$$
$$m_1+m_1\rightarrow {}^*m_2{}^*, \quad (1u, 2)$$
$$m_1+c^*\rightarrow cm_1{}^*, \quad (1c, 1)$$
$$m_1+c\rightarrow {}^*m_1{}^*+c, \quad (1c, 2)$$
$$m_1+cc\rightarrow cm_1{}^*+c^*, \quad (1c, 3)$$
$$m_1+s\rightarrow {}^*m_1{}^*+s, \quad (1s, 1)$$
$$m_1+ss_1\rightarrow sm_1{}^*+s_1 \quad (1s, 2)$$
$$m_1+m_j\rightarrow {}^*m_1{}^*+m_j. \quad (1p, 1)$$

* We shall use the following symbols to distinguish different reaction steps: The first index 1 indicates always activation processes. If they are uncatalyzed, it is followed by *u*, if they are catalyzed by *c*; if they are effected by the solvent *s*, and if affected by a polymer *p* is added. Hence we get the classes (1*u*), (1*c*), (1*s*), and (1*p*). If there are several cases in one class, a third index 1, 2, ⋯ is added.

[10] M. Polyani, *Atomic Reactions* (University of London Press, London, 1932); F O. Rice and K. K. Rice, *The Aliphatic Free Radicals* (Johns Hopkins Press, Baltimore, 1935).

[11] R. M. Thomas, W. J. Sparks, P. K. Frolich, M. Otto, and M. Muller-Cunradi, J. Am. Chem. Soc. **62**, 276 (1940).

[12] G. Williams, J. Chem. Soc. London **1938**, 246, 1046 (1938); **1940**, 775 (1940).

† It has to be mentioned that (1*c*, 1) and (1*c*, 3) are not true catalytical processes, because the catalyst takes part permanently in the reaction, and—as found experimentally—appears at one or both ends of the final chain-molecules. (1*c*, 2), however, might be regarded as catalysis according to the usual definition of the word.

** According to this nomenclature, we shall use the following notation for the rate constants: Reaction (1*u*, 1) has the rate constant ${}^1k_{1u}$, reaction (1*s*, 2) the constant ${}^2k_{1s}$, etc.

It can be seen that two altogether different types of nuclei can be formed. In case (1*c*, 1), (1*c*, 3), and (1*s*, 2), we get a particle having an unpaired or odd electron, which can only be disposed of by pairing up (saturating its spin) with another odd electron provided by another particle (atom or radical). In all other cases, the activated nucleus contains two unpaired electrons, which have been brought into this excited (triplet) state by transfer of sufficient energy during the collision. Such activated nuclei (biradicals) are much more accessible to deactivation than the radicals (1*c*, 1), (1*c*, 3), and (1*s*, 2). Any collision which removes sufficient energy may bring the molecule back in its singlet ground state (closed double bond). It is true that the *a priori* probability of such a triplet-singlet transition is small, but in the presence of perturbation which is always materialized during a collision, the frequency factor may well be brought up from a value of around 10^5 to its normal value of 10^{11} or 10^{12}.

It is therefore to be expected that nuclei of this type are much more sensitive to deactivation as compared with the radicals (1*c*, 1), (1*c*, 3), and (1*s*, 2), and it seems advisable to distinguish between *deactivation* by energy removal and *termination* by electron pairing. It will be shown later that experimental evidence favors this distinction and that accordingly we have to consider two types of inhibitors: those which catalyze the singlet-triplet transition, and those which take care of an unpaired electron.

Finally it should be noticed that (1*u*, 2) will also be comparatively difficult to deactivate, because the closure of the two free valencies involves either the migration of a hydrogen atom or the formation of a four membered ring. Both processes require additional energy supply and are therefore presumably less frequent than the simple closure of the activated double bond in (1*u*,1; 1*c*, 1; 1*s*, 1; and 1*p*, 1).

We shall, therefore, introduce the following deactivation processes* which may destroy active centers before they even have a chance to grow into a short chain (such as a dimer or trimer):

$$\begin{aligned} {}^*m_1{}^*+m_1 &\rightarrow m_1+m_1, && (u)\ (k_{4u}) \\ {}^*m_1{}^*+c &\rightarrow m_1+c, && (c)\ (k_{4c}) \\ {}^*m_1{}^*+s &\rightarrow m_1+s && (s)\ (k_{4s}) \\ {}^*m_1{}^*+m_j &\rightarrow m_1+m_j. && (p)\ (k_{4p}) \end{aligned} \qquad (4)$$

In these processes *pairs* of asterisks attached to one molecule are destroyed, which corresponds to the closure of the double bond.

Propagation in the form of chain growth, takes place by monomer addition to any of the active centers, as indicated by an asterisk in such a way that the number of asterisks on both sides of the equations are equal: activation is *maintained* during chain growth.

Such processes are:

$$\begin{aligned} cm_1{}^*+m_1 &\rightarrow cm_2{}^*, && (g, 1)\ ({}^1k_{2g}) \\ cm_j{}^*+m_1 &\rightarrow cm_{j+1}^* \\ {}^*m_1{}^*+m_1 &\rightarrow {}^*m_2{}^* \\ {}^*m_j{}^*+m_1 &\rightarrow {}^*m_{j+1}^* && (g, 2)\ ({}^2k_{2g}) \end{aligned} \qquad (2)$$

(2*g*, 1) represents growth of the chain in *one* direction in such a way that a fragment of the catalyst appears at one end of the chain, while (2*g*, 2) describes chain growth in *two* directions. It seems that both types have been observed experimentally.[13]

There are, however, other, less simple processes which also leave the number of asterisks on the two sides of the equations unchanged and hence can be classified as propagation steps. They are:

(*a*) Chain transfer.

$$\begin{aligned} cm_j{}^*+m_1 &\rightarrow cm_j+m_1{}^*, && (t, 1)\ ({}^1k_{2t}) \\ {}^*m_j{}^*+m_1 &\rightarrow {}^*m_j+m_1{}^*. && (t, 2)\ ({}^2k_{2t}) \end{aligned} \qquad (2)$$

It has been found experimentally that chain transfer can be catalyzed by certain substances (i.e., CCl_4) in such a way that one part (*t*) of the transfer catalyst (*tr*) terminates one chain, while the rest of it (*r*) originates another. This

* As the first index 2 is already in use for propagation reactions, we suggest maintaining this use to characterize termination processes with 3 and deactivation processes with 4. The symbols *u*, *c*, *s*, and *p* are used as above.

[13] J. Abere, G. Goldfinger, H. Naidus, and H. Mark, Paper presented at the American Chemical Society Meeting in Buffalo on September 9, 1942; H. Pfann, Thesis, Brooklyn Polytechnic Institute (May, 1942); C. C. Price and R. W. Kell, J. Am. Chem. Soc. **63**, 2798 (1941); C. C. Price, R. W. Kell, and E. Krebs, J. Am. Chem. Soc. **64**, 1103 (1942); C. C. Price and D. A. Durham, J. Am. Chem. Soc. **64**, 2508 (1942).

can be represented by:

$$cm_j^* + tr \rightarrow cm_jt + r^*, \quad (tr, 1) \quad ({}^1k_{2tr})$$
$$*m_j^* + tr \rightarrow *m_jt + r^*. \quad (tr, 2) \quad ({}^2k_{2tr}) \qquad (2)$$

(*b*) Branching. As we do not have more than preliminary experimental indication for branching of polyvinyl derivatives and no quantitative measurements as to its amount, we shall not include branching in this publication, but wait until further experimental development allows us to check formulas which can be derived in a similar way as shown for polymerization without branching in Part III.

Termination or *cessation* destroys single active centers by providing for their odd electrons to pair up with other impaired electrons. The most frequent elementary processes of this type are:

$$*m_j^* + *m_k^* \rightarrow *m^*_{j+k}, \quad (u) \quad (k_{3u})$$
$$cm_j^* + c^* \rightarrow cm_jc, \quad (c, 1) \quad ({}^1k_{3c})$$
$$cm_j^* + cm_k^* \rightarrow cm_{j+k}c. \quad (c, 2) \quad ({}^2k_{3c}) \qquad (3)$$

In these processes, *pairs* of asterisks disappear, but in such a way that each of them is contributed by another particle. This corresponds to the pairing of odd electrons belonging to different molecules. In case (3*u*), two chains saturate each other with one of their ends, hence two asterisks are still free on the right-hand side. If all four active centers would disappear, we would obtain m_{j+k}, which represents a saturated ring having $(j+k)$ monomers.

Termination can also be effected by certain molecules *b*, which have the capability to dispose of an unpaired electron, without providing another unpaired electron (aromatic hydroxyl and nitro compounds, etc.).

$$cm_j^* + b \rightarrow cm_j + b, \quad (b, 1) \quad ({}^1k_{3b})$$
$$*m_j^* + b \rightarrow m_j^* + b. \quad (b, 2) \quad ({}^2k_{3b}) \qquad (3)$$

There seem to be still other cessation reactions possible, such as exchange of hydrogen atoms or reaction with the wall or with suspended particles, but we shall not include them in the following calculations, as there is little or no quantitative experimental evidence for them at present.

III. SOME KINETIC CONSIDERATIONS

Activation in general will be given by

$$\frac{dcm_1^*}{dt} = {}^1k_{1c}m_1c^* + {}^2k_{1c}m_1cc, \qquad (5a)$$

$$\frac{d^*m_1^*}{dt} = m_1({}^1k_{1u}m_1 + {}^2k_{1c}c + {}^1k_{1s}s + {}^1k_{1p}p), \qquad (5b)$$

$$\frac{d^*m_2^*}{dt} = {}^2k_{1u}m_1^2, \qquad (5c)$$

where, on the right-hand side the different contributing terms are enumerated. If one, or two, of them are preponderant, it will be justified to neglect the others. As soon as an active nucleus is produced, two processes (in general) compete for it: the *deactivation*, which destroys it again, and the *propagation*, which builds it up into a chain. No deactivation,* however, can affect the nuclei produced by the terms $({}^1k_{1c})$, $({}^3k_{1c})$, and $({}^2k_{1s})$ in (1*c*) and hence, we have to express the rate of deactivation by

$$-\frac{d^*m_1^*}{dt} = *m_1^*(k_{4u}m_1 + k_{4c}c + k_{4s}s + k_{4p}p). \qquad (6)$$

Propagation is represented by

$$\frac{dcm^*_{j+1}}{dt} = k_{2g}cm_j^*m_1, \qquad (7a)$$

$$\frac{d\,*m^*_{j+1}}{dt} = k_{2g}\,*m_j^*\,m_1, \qquad (7b)$$

and *chain transfer* by

$$\frac{dm_1^*}{dt} = {}^1k_{2t}cm_j^*m_1, \qquad (8a)$$

$$\frac{dm_1^*}{dt} = {}^2k_{2t}\,*m_j^*\,m_1. \qquad (8b)$$

It will be noticed that the rate constants $({}^1k_{2g})$ and $({}^2k_{2g})$ for normal propagation have been assumed to be equal, namely (k_{2g}). This means that propagation is assumed to be independent of whether the chain grows in one or two

* Note that deactivation involves the disappearance of a *pair* of asterisks from the *same* molecule.

directions and also independent of the chain length. There seems to be experimental support for this simplification. The same is true for chain transfer.

Termination finally can be expressed by

$$-\frac{dcm_j^*}{dt}=cm_j^*({}^1k_{3c}c+{}^2k_{3c}\Sigma cm_i^*+{}^1k_{3b}b), \quad (9a)$$

$$-\frac{d^*m_j^*}{dt}={}^*m_j^*(k_{3u}\Sigma\,{}^*m_i^*+{}^2k_{3b}b). \quad (9b)$$

From these equations, we obtain for the steady state concentration of $*m_1*$ (active nuclei being sensitive against deactivation)

$${}^*m_1^*=\frac{m_1({}^1k_{1u}m_1+{}^2k_{1c}c+{}^1k_{1s}s+{}^1k_{1p}p)}{m_1(k_{2g}+k_{4u})+k_{4c}c+k_{4s}s+k_{4p}p}, \quad (10a)$$

and for cm_1^* (active nuclei being unsensitive against deactivation)

$$cm_1^*=\frac{{}^1k_{1c}c^*+{}^2k_{1c}cc}{k_{2g}}. \quad (10b)$$

Furthermore, we get for the steady state concentration of active centers, incorporated in growing chains having already attained a certain length

$$\Sigma\,{}^*m_j^*={}^*m^*=\frac{k_{2g}m_1{}^2({}^1k_{1u}m_1+{}^2k_{1c}c+{}^1k_{1s}s+{}^1k_{1p}p)}{(k_{3u}\,{}^*m^*+{}^2k_{3b}b)(k_{2g}m_1+k_{4u}m_1+k_{4c}c+k_{4s}s+k_{4p}p)}, \quad (11a)$$

$$\Sigma cm_j^*=cm^*=\frac{{}^1k_{1c}c^*+{}^2k_{1c}cc}{({}^1k_{3c}c+{}^2k_{2c}cm^*+{}^1k_{3b}b)}. \quad (11b)$$

Solving these two equations for $*m^*$ and cm^*, respectively, one obtains

$${}^*m^*=\frac{1}{2k_{3u}}\left[\left({}^2k_{3b}{}^2b^2+4k_{2g}k_{3u}m_1{}^2\frac{{}^1k_{1u}m_1+{}^1k_{1c}c+{}^1k_{1s}s+{}^1k_{1p}p}{k_{2g}m_1+k_{4u}m_1+k_{4c}c+k_{4s}s+k_{4p}p}\right)^{\frac{1}{2}}-{}^2k_{3b}b\right], \quad (12a)$$

$$cm^*=\frac{1}{2k_{3c}}\{[({}^1k_{3c}c^*+{}^1k_{3b}b)^2+4k_{3c}k_{1c}m_1c^*]^{\frac{1}{2}}-({}^1k_{3c}c^*+{}^1k_{3b}b)\}. \quad (12b)$$

In the following we shall abbreviate the bracket term in (12*a*) with $B(a)$ and the bracket in (12*b*) with $B(b)$.

From these steady state concentrations of the growing centers we can now derive *two* experimentally measurable quantities, namely, the initial rate R with which the monomer is consumed (over-all rate of the reaction) and the initial number average degree of polymerization $\bar{P}_n$ of the polymer formed.

Considering that the rate of monomer consumption is proportional to the product of the concentrations of the monomer, and of the active uncatalyzed centers we obtain for the uncatalyzed reaction:

R(initial, uncatalyzed)

$$=m_1\left[({}^1k_{1u}m_1+{}^1k_{1c}c+{}^1k_{1s}s+{}^1k_{1p}p)-\frac{k_{2g}}{2k_{3u}}B(a)\right] \quad (13a)$$

and for the catalyzed reaction:

R(initial, catalyzed)

$$=m_1\left[{}^1k_{1c}c^*-\frac{k_{2g}}{2k_{3c}}B(b)\right]. \quad (13b)$$

The number average degrees of polymerization are

$\bar{P}_n$(uncatalyzed)

$$=\frac{{}^1k_{1u}m_1+{}^1k_{1c}c+{}^1k_{1s}s+{}^1k_{1p}p+\frac{k_{2g}}{2k_{3u}}B(a)}{{}^1k_{1u}m_1+{}^1k_{1c}c+{}^1k_{1s}s+{}^1k_{1p}p+\frac{{}^2k_{2t}}{2k_{3u}}B(a)}, \quad (14a)$$

$$\bar{P}_n(\text{catalyzed})=\frac{{}^1k_{1c}c^*+{}^2k_{1c}cc+\frac{k_{2g}}{2k_{3c}}B(b)}{{}^1k_{1c}c^*+{}^2k_{1c}cc+\frac{{}^1k_{2t}}{2k_{2c}}B(b)}. \quad (14b)$$

IV. DISCUSSION OF SOME EXPERIMENTAL RESULTS

It is not the purpose of this paper to discuss fully the techniques and results obtained in our experimental investigations. We wish merely to indicate the general agreement between some of the more representative data and the theory as outlined above.

Figure 1 shows the intrinsic viscosities of initially formed polymers for three initial monomer concentrations in toluene at 100°C plotted against the reciprocal square root of the catalyst concentration as added. It can be seen that the four measured points for the lowest (10 percent) monomer concentration are arranged with reasonable accuracy on a straight line, while for the two higher concentrations (20 percent and 40 percent) the straight line bends toward the abscissae at lower catalyst concentrations.

It seems that the equations derived above permit the following interpretation of this behavior:

Assuming first that the intrinsic viscosity (over the limited range under consideration) is proportional to the weight (viscosity) average degree of polymerization, which in turn is proportional to the number average, we expand equation (14*b*) and neglecting terms of higher order obtain

$$\bar{P}_n(\text{catalyzed}) = \frac{k_{2g}m_1 + {}^1k_{3c}c^*}{{}^1k_{2t}m_1 + {}^1k_{3c}c^* + {}^1k_{3b}b}. \qquad (15)$$

Assuming further that the concentration of retarders or inhibitors of the type b is small we can further simplify (15) and get

$$\bar{P}_n(\text{catalyzed}) = \frac{k_{2g}m_1 + {}^1k_{3c}c^*}{{}^1k_{2t}m_1 + {}^1k_{3c}c^*}. \qquad (16)$$

At very high catalyst concentration [very low values of $1/(c_k)^{\frac{1}{2}}$] this reduces to unity, which corresponds to a very small value for the intrinsic viscosity. As a matter of fact all three curves of Fig. 1 intersect the ordinate at values below $\eta_i = 0.04$. At lower concentrations of the catalyst the shape of (15) depends upon the magnitude of all three quantities on the right side. In general k_{2g} will be large compared with ${}^1k_{2t}$, otherwise no high polymer would be formed at all. At small monomer concentrations we can therefore neglect ${}^1k_{2t}m_1$ but not $k_{2g}m_1$ at the side of ${}^1k_{3c}c^*$. Then the relation

$$\bar{P}_n(\text{catalyzed}) = 1 + \frac{k_{2g}m_1}{{}^1k_{3c}c^*} \qquad (17)$$

is obtained, which calls for a straight line in the plot of Fig. 1, where c^* is proportional to the square root of the catalyst as added. It can be seen that, in fact, the curve for the lowest monomer concentration employed is nearest to a straight line. At higher monomer concentrations ${}^1k_{2t}m_1$ cannot be neglected and chain transfer makes itself felt. It reduces the degree of polymerization and with it the intrinsic viscosity of the polymer initially formed below the value as extrapolated from the initial straight lines. The curvature of the curve in Fig. 1 permits the determination of the rate constant for chain transfer, if the constants for propagation and termination are known.

At very high catalyst concentrations the concentration of the monomer should have no influence on $\bar{P}_n$ and all three extrapolated straight lines should intersect the ordinate at the same point. This is not exactly true in the graph, but is at least indicated with reasonable approximation.

Figure 2 contains the initial rates of polymer formation (which is equal to monomer consumption) as functions of monomer concentration at three initial catalyst concentrations in toluene at 100°C. Equation (13*b*) shows that omitting

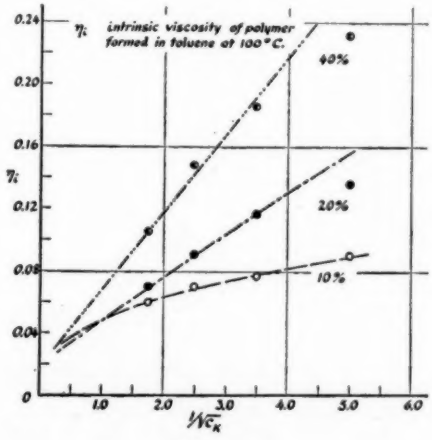

FIG. 1.

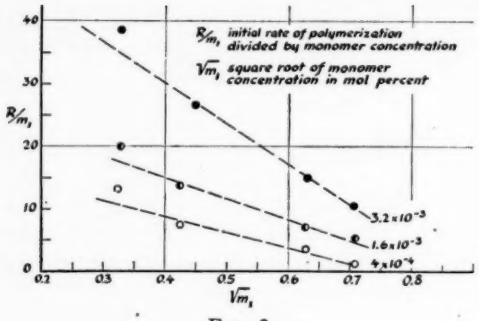

FIG. 2.

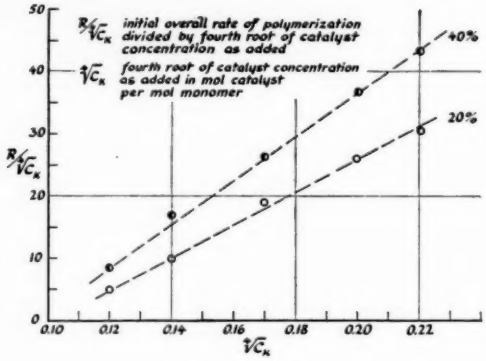
$R/\sqrt{C_K}$, initial overall rate of polymerization divided by fourth root of catalyst concentration as added
$\sqrt[4]{C_K}$, fourth root of catalyst concentration as added in mol catalyst per mol monomer
40%
20%
$R/\sqrt{C_K}$
$\sqrt[4]{C_K}$

FIG. 3.

terms with b, this initial rate should be

$$R(\text{initial, catalyzed}) = {}^1k_{1c}m_1c^* + \frac{k_{2g}m_1}{2\,{}^2k_{3c}}[-{}^1k_{3c}c^* + ({}^1k_{3c}^2c^{*2} + 4\,{}^2k_{3c}k_{1c}m_1c^*)^{\frac{1}{2}}]. \quad (18)$$

At low monomer concentrations the second term under the square root can be neglected and the over-all rate reduces to $k_{1c}m_1c^*$, while at higher values for m_1, the first term can be neglected and one obtains

$$R(\text{initial}) = {}^1k_{1c}m_1c^* + k_{2g}\left(\frac{{}^1k_{1c}}{{}^2k_{3c}}\right)^{\frac{1}{2}} m_1^{\frac{1}{2}}c^{*\frac{1}{2}}. \quad (19)$$

Plotting R/m_1 against $m_1^{\frac{1}{2}}$ one is expected to have a straight line, the deviations of which are caused by the neglections in going from Eq. (13b) to Eq. (19). Figure 2, being such a graph, shows that, in fact, at higher monomer concentrations (20, 40, and 50 mole percent monomer) a straight line is reasonably approximated. At low values for m_1, however, noticeable deviations take place.

Figure 3, finally, shows the influence of catalyst concentration. Plotting R divided by $(c^*)^{\frac{1}{2}}$ against $(c^*)^{\frac{1}{2}}$ one should again expect a straight line from Eq. (19). In Fig. 3, R divided by the fourth root of the catalyst as added is plotted on the ordinate *versus* the fourth root on the abscissae for two relatively high monomer concentrations (20 percent and 40 percent). The points fall with fair approximation on straight lines.

This approximate comparison of our experimental values with Eq. (14) and (19) together with the previous results of other authors as referred to in footnote 2 seem to indicate that the steady state approximation can be legitimately used to describe the chain mechanism of styrene polymerization if the various parameters (monomer concentration, catalyst concentration, temperature) are varied in limits as indicated above.

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The Kinetic Theory of Rubber

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The (isothermal) Young's modulus of *ideal* rubber is determined by statistical methods. The macro-state of a chain-molecule is here defined in terms of its length and not in terms of the distance between the ends of the chain. Section 1 deals with thermodynamical results holding for ideal rubber and in Section 2 the treatment based on ends-separation of the molecule-chain is described. Section 3 treats the problem on the basis of the length of the molecule-chain.

1.

THE marked difference between the elastic properties of rubber and a metal is well known, for not only are the elastic moduli in the case of rubber of a far smaller magnitude than those for a metal, but also, whereas in the case of a metal the tension of a stretched wire decreases with rise of temperature, in the case of rubber when heated in the expanded state the tension in general increases. The behavior of rubber is similar to that of a compressed gas for which the pressure (at constant volume) increases with temperature. This similarity between a gas and rubber is not merely superficial, but is the expression of the underlying fact that in both cases the elastic behavior is primarily due to the thermal motions of the molecules. For the purposes of a statistical treatment a molecule of rubber is considered as a chain of a large number of links—the links being free to rotate about their junctions. Because of the thermal motions any molecular chain will be in constant sinuous motion; the shape of the chain will be changing from moment to moment just as the position of a molecule in a gas because of the thermal motion changes from moment to moment.

The basis of any statistical treatment is to enumerate the number of complexions corresponding to a given macroscopic state (i.e., the number of micro-states which all generate the same given macro-state), and then to derive entropy with the help of Boltzmann's relation connecting entropy and probability. Several investigators particularly Mark,[1] Pelzer,[2] and Wall[3] have made important contributions to this subject. In their treatment the macro-state of the molecule is defined by fixing the distance between the ends of the molecule-chain. In this paper we shall follow a different procedure in that *the macro-state is defined not in terms of the ends-separation but, what appears more reasonable, in terms of the length (or extent) of the chain.* In Section 2 the treatment (according to Wall) based on ends-separation is summarized, and Section 3 deals with the treatment based on the length of the chain.

In theoretical investigations on the elasticity of rubber it is usual to consider an *ideal* rubber which is defined by the property that

$$(\partial U/\partial l)_T=0, \tag{1}$$

where U is the internal energy and l the length of the rubber piece. This relation corresponds to Joule's law for the case of a perfect gas which states that the internal energy of an ideal gas is independent of the volume and depends only on the temperature. The approximate validity of Joule's law for a rubber sample has been established by the investigations of Meyer and Ferri.[4] From the thermodynamic point of view it is significant that gases and rubber both approximately obey Joule's law. An immediate consequence of this is that if a rubber piece of unstretched length l_0 be stretched to a length l by subjecting it to a tensile stress Γ, then, Γ and l

[1] H. Mark, *High Polymers*, Interscience Publishers, New York, 1940), p. 69.
[2] H. Pelzer, *Reports on Progress in Physics* (Physical Society, London, 1940) Vol. 6, p. 330.
[3] F. T. Wall, J. Chem. Phys. **10**, 132 (1942); also E. Guth and H. M. James, Ind. Eng. Chem. **33**, 624 (1941); **34**, 1365 (1942); Phys. Rev. **59**, 111 (1941).
[4] K. H. Meyer and C. Ferri, Helv. Chim. Acta **18**, 570 (1935); also R. L. Anthony, R. H. Caston, E. Guth, and L. E. Peterson, Ind. Eng. Chem. **34**, 1349 (1942); J. Phys. Chem. **46**, 826 (1942).

must be connected by a relation of the form

$$\Gamma = Tf(l), \tag{2}$$

where T is the absolute temperature and $f(l)$ is some function of length l only. For, if dS denotes the increase in entropy, we have

$$dU = TdS + \Gamma dl,$$

or

$$\Gamma = \left(\frac{\partial U}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T,$$

and using (1)

$$\Gamma = -T\left(\frac{\partial S}{\partial l}\right)_T. \tag{3}$$

If we use the thermodynamic relation

$$\left(\frac{\partial S}{\partial l}\right)_T = -\left(\frac{\partial \Gamma}{\partial T}\right)_l, \tag{4}$$

we have*

$$\Gamma = Tf(l).$$

As Γ depends only on the change in length, we may write

$$\Gamma = Tf(l) = TF(l/l_0),$$

where l_0 is the unstretched length. When the stress is small Γ will be proportional to $(l-l_0)/l_0$ and, thus in the region where Hooke's law is valid, (2) reduces to

$$\Gamma = TR'\frac{l-l_0}{l_0}, \tag{5}**$$

where R' is a constant. The object of the statistical theory is to determine:

(i) the value of the constant R' in terms of chain-length and the molecular weight of rubber, and (ii) the form of $F(l/l_0)$, particularly when l/l_0 is large.

2.

The starting point of the usual statistical theory of rubber is the probability relation (well known in the discussion of Brownian motion)

$$p(x)dx = A \exp\left(-\frac{x^2}{2\lambda b}\right)dx, \tag{6}$$

where $p(x)dx$ denotes the probability that the distance between the two ends of a chain of v links, each of length $b=\lambda/v$, lies between the limits x and $x+dx$. The normalization constant A is given by

$$\int_0^\infty p(x)dx = 1, \quad \text{or} \quad A = \frac{2}{(2\pi\lambda b)^{\frac{1}{2}}}. \tag{7}$$

We shall consider throughout in this paper only the one-dimensional case, i.e., we shall assume the chain to lie entirely along the x direction. The generalization to three dimensions is easily made, but that will not be discussed here. The object of the present paper is to describe the statistical theory of rubber in terms of the length of the molecule-chain, and to compare this approach with the usual one which is based not on the chain-length but on the ends-separation. (The chain-length ρ should not be confused with $\lambda=vb$ which denotes the length of a fully extended chain. Because of the folding of the chain, ρ in general will be extremely small compared to λ.)

Let us now consider an assembly of a large number N of similar molecule-chains. Let $N(x)dx$ denote those chains of the assembly which have their ends-separation lying in the interval $(x, x+dx)$. To be precise, we cannot take x to be a continuous variable, for it will vary discontinuously in steps of b, and, therefore, to discuss the statistical distribution we suppose the interval of length λ divided into a large number of zones or cells such that the size of any cell is large compared to b and yet very small compared to λ. Let the rth cell correspond to the interval x_r to x_r+dx_r, and let N_r denote the number of molecule-chains, having their ends-separation lying within the above interval, then, we have

$$\sum_r N_r = N,$$

and

$$\sum_r x_r N_r = \bar{x}N, \tag{8}$$

where $\bar{x}$ is the average ends-separation.

Consider a distribution defined by the numbers $(N_1, N_2, \cdots, N_r, \cdots)$. The number of ways of

* Thus, for ideal rubber the temperature-coefficient of increase of tension for constant length is $\frac{1}{\Gamma}\left(\frac{\partial \Gamma}{\partial T}\right)_l = \frac{1}{T}$.

** The length l_0 may be supposed to correspond to the term "b" in van der Waals' equation for a gas.

realizing this distribution will be given by

$$W=N!\prod_r \frac{p_r^{N_r}}{N_r!}, \tag{9}$$

when p_r is the probability of a chain being contained in the rth cell; i.e., p_r is the probability that the ends-separation lies within the interval (x_r, x_r+dx_r). We have from (6)

$$p_r=A\exp\left(-\frac{x_r^2}{2\lambda b}\right)dx_r; \quad \sum p_r=1. \tag{10}$$

We shall first determine the value of N_r for the most probable distribution, i.e., *the distribution for which W is a maximum*. By differentiating (9), or even otherwise, it follows that for the most probable distribution

$$\bar{N}_r=Np_r, \tag{11}$$

where a bar over a symbol denotes its value for the most probable distribution. The maximum value of W is given by,

$$\bar{W}=N!\prod_r \frac{(p_r)^{Np_r}}{(Np_r)!}. \tag{12}$$

From (9) and (12) we obtain, after using Sterling's theorem,

$$W=N^N(2\pi N)^{\frac{1}{2}}\prod_r\left(\frac{p_r}{N_r}\right)^{N_r}\frac{1}{(2\pi N_r)^{\frac{1}{2}}},$$

and

$$\bar{W}=\frac{(2\pi N)^{\frac{1}{2}}}{\prod_r(2\pi Np_r)^{\frac{1}{2}}},$$

and, therefore, introducing Boltzmann's theorem, we have for the decrease of entropy S,

$$\begin{aligned}\frac{S-\bar{S}}{k}&=\log\frac{W}{\bar{W}}\\&=\sum_r(N_r+\tfrac{1}{2})\log\frac{Np_r}{N_r}\\&=\sum_r(N_r+\tfrac{1}{2})\log\frac{\bar{N}_r}{N_r}\doteq\sum_r N_r\log\frac{\bar{N}_r}{N_r},\end{aligned} \tag{13}$$

where k is the Boltzmann constant. As $\bar{W}$ is the maximum value of W, $\log(W/\bar{W})\leqslant 0$. Equation (13) is an important one as it gives the decrease in entropy in passing from the most probable distribution (sometimes referred to as $\bar{W}$-distribution) to any other distribution. As an illustration consider a distribution which differs from the most probable distribution only as regards the population in the rth and sth cells: $N_r=\bar{N}_r+1$, $N_s=\bar{N}_s-1$, then, we have

$$\begin{aligned}\frac{S-\bar{S}}{k}&=\log\frac{W}{\bar{W}}=(\bar{N}_r+1)\log\frac{\bar{N}_r}{\bar{N}_r+1}\\&\quad+(\bar{N}_s-1)\log\frac{\bar{N}_s}{\bar{N}_s-1}\sim-\frac{1}{N}\left(\frac{1}{p_r}+\frac{1}{p_s}\right).\end{aligned}$$

The application of Eq. (13) to the case of rubber is made in the following manner. The unstretched state of rubber is identified with the state of maximum probability. The entropy of ideal rubber in the region of Hooke's law is given by, using (4) and (5),

$$S=\psi(T)+\int_{l_0}^{l}\left(\frac{\partial S}{\partial l}\right)_T dl=\psi(T)-R'\frac{(l-l_0)^2}{2l_0}, \tag{14}$$

where $\psi(T)$ is a function of temperature only. The entropy is thus, for a given T, maximum for $l=l_0$.

The probability W for the stretched state is determined by assuming that when rubber is stretched from its original length l_0 to $l=\alpha l_0$, then, the ends-separation of every molecule-chain is also increased in the same ratio.* For the stretched state the rth cell will contain chains that originally in the unstretched state had their ends-separation lying in the range x_r/α to $(x_r+dx_r)/\alpha$, so that after stretching from l_0 to $l=\alpha l_0$, the ends-separation lies in the interval x_r to x_r+dx_r. The value N_r, therefore, is equal to the number of chains which in the most probable distribution (i.e., unstretched state) have their ends-separation in the interval x_r/α to $(x_r+dx_r)/\alpha$, and hence from (10) and (11) we have,

$$\begin{aligned}N_r&=\left(\frac{2}{\pi b\lambda}\right)^{\frac{1}{2}}N\exp\left(-\frac{x_r^2}{2\lambda b\alpha^2}\right)\frac{dx_r}{\alpha}\\&=\frac{\bar{N}_r}{\alpha}\exp\left(-\frac{x_r^2}{2\lambda b}\right)\left(\frac{1}{\alpha^2}-1\right).\end{aligned} \tag{15}$$

*We of course ignore the extremely small number of molecules whose ends-separation already in the unstretched state is comparable to λ.

Thus we have

$$\frac{S-\bar{S}}{k}=\sum_r N_r \log \frac{\bar{N}_r}{N_r}$$
$$=\sum_r N_r\left\{\log \alpha+\frac{x_r^2}{2\lambda b}\left(\frac{1}{\alpha^2}-1\right)\right\},$$

which using (15), and replacing the sum by an integral reduces to

$$\frac{S-\bar{S}}{k}=N\log\alpha-\frac{N(\alpha^2-1)}{2\lambda b}\frac{2}{(2\pi\lambda b)^{\frac{1}{2}}}$$
$$\times\int_0^\infty \exp\left(-\frac{x^2}{2\lambda b\alpha^2}\right)\frac{x^2}{\alpha^2}\frac{dx}{\alpha},$$
$$=N\log\alpha-\frac{2N(\alpha^2-1)}{\pi^{\frac{1}{2}}}\int_0^\infty z^2\exp(-z^2)dz,$$

or we have

$$S-\bar{S}=Nk\left\{\log l/l_0-\frac{l^2-l_0^2}{2l_0^2}\right\}. \qquad (16)$$

Therefore, we obtain

$$\Gamma=-T\left(\frac{\partial S}{\partial l}\right)_T=-NkT\left\{\frac{1}{l}-\frac{l}{l_0^2}\right\}$$
$$=\frac{NkT}{ll_0^2}(l+l_0)(l-l_0). \qquad (17)$$

The Young's modulus (γ) for the isothermal case is given by

$$\gamma=l\left(\frac{\partial T}{\partial l}\right)_T=NkT\left(\frac{1}{l}+\frac{l}{l_0^2}\right),$$

and if d_0 denotes the density of rubber in the unstretched state and M the molecular weight of a molecule-chain, we have

$$\gamma=\frac{RTd_0}{M}\left(\frac{l_0}{l}+\frac{l}{l_0}\right)\sim\frac{2RTd_0}{M}, \qquad (18)^*$$

where R is the gas constant.

3.

We shall now develop, following Section 2 with necessary alterations, the statistical treatment by defining the macro-state of a molecule-chain in terms of its length. It is improbable that a molecule-chain will be found in a completely unfolded condition, but, on the other hand, it will be folded at many of its junctions, and, therefore, in general, the length of the chain will be much smaller than its uncoiled length λ. The probability $p(\rho)d\rho$ that the length of the chain lies between ρ and $\rho+d\rho$ is given by the following expression (when the number of links v is large) which has been derived by Daniels[5] in a recent paper:

$$p(\rho)d\rho=\frac{8}{(2\pi b\lambda)^{\frac{1}{2}}}\sum_{s=1}^{\infty}(-)^{s-1}s^2\exp\left(-\frac{s^2\rho^2}{2b\lambda}\right)d\rho, \qquad (19)$$
$$\int_0^\infty p(\rho)d\rho=1,$$

b being the length of each link, and $\lambda=vb$. Using the properties of ϑ-functions, Eq. (19) may be transformed into the following form which is more convenient for small value of ρ:

$$p(\rho)d\rho=\frac{8b\lambda}{\rho^5}\sum_1^\infty\{-\rho^2+\pi^2b\lambda(2s-1)^2\}$$
$$\times\exp\left(-\frac{(2s-1)^2\pi^2b\lambda}{2\rho^2}\right)d\rho. \qquad (20)$$

The asymptotic expressions for the two limiting cases are, for $\rho\to0$

$$p(\rho)d\rho=\frac{8\pi^2b^2\lambda^2}{\rho^5}\exp\left(-\frac{\pi^2b\lambda}{2\rho^2}\right)d\rho, \qquad (21)$$

and for $\rho\to\infty$

$$p(\rho)d\rho=\frac{8}{(2\pi\lambda b)^{\frac{1}{2}}}\exp\left(-\frac{\rho^2}{2b\lambda}\right)d\rho. \qquad (22)$$

It may be remarked here that, whereas the most probable ends-separation of a molecule-chain is *zero*, the most probable value for the length of the chain is $1.346(\lambda b)^{\frac{1}{2}}$. Moreover, almost all the chains have their lengths lying in the interval $(0.5(\lambda b)^{\frac{1}{2}}, 3.5(\lambda b)^{\frac{1}{2}})$. The average value of ρ as obtained from (19) is $\bar{\rho}=2(2\lambda b/\pi)^{\frac{1}{2}}=1.596(b\lambda)^{\frac{1}{2}}$, whereas the average value of the ends-separation

* Equation (18) is identical with (19) of Wall (reference 3).

[5] H. E. Daniels, Proc. Camb. Phil. Soc. **37**, 244 (1941).

is

$$\overline{|x|} = (2\lambda b/\pi)^{\frac{1}{2}} = 0.7979(\lambda b)^{\frac{1}{2}} = \bar{\rho}/2.$$

Let us consider a statistical assembly of a large number of chains at temperature T, and let N_r denote the number of chains having their lengths lying within the interval ρ_r to $\rho_r+d\rho_r$. The number (W) of ways in which a distribution $(N_1, N_2, \cdots, N_r, \cdots)$ of the assembly can be realized is given by

$$W = N! \prod_r \frac{p_r^{N_r}}{N_r!}, \tag{23}$$

$$\sum_r N_r = N. \tag{24}$$

In (23), p_r denotes the probability that the length of a molecule-chain lies in the interval $(\rho_r, \rho_r+d\rho_r)$, i.e., we write p_r for $p(\rho_r)d\rho_r$. From (23) and (24) it follows, as in Section 2, that the most probable distribution is given by

$$N_r = \bar{N}_r = Np_r; \tag{25}$$

and if $\bar{W}$ denotes the corresponding value of W, we obtain for the decrease of entropy S,

$$\frac{S-\bar{S}}{k} = \sum_r N_r \log \frac{\bar{N}_r}{N_r}. \tag{26}$$

When rubber is stretched from its original length l_0 to $l=\alpha l_0$, let us assume that the length of each molecule-chain is also increased α times.* In the stretched state the rth cell will contain chains which in the unstretched state, had their lengths between ρ_r/α and $(\rho_r+d\rho_r)/\alpha$.

Therefore, we have

$$N_r = Np\left(\frac{\rho_r}{\alpha}\right)\frac{d\rho_r}{\alpha}, \tag{27}$$

and using (25), and (26) we obtain

$$\begin{aligned}\frac{S-\bar{S}}{k} &= N\int_0^\infty p\left(\frac{\rho}{\alpha}\right)\log\frac{\alpha p(\rho)}{p(\rho/\alpha)}\frac{d\rho}{\alpha}\\ &= N\int_0^\infty p(\rho)\log\frac{\alpha p(\alpha\rho)}{p(\rho)}d\rho\\ &= N\left\{\log\alpha_1\int_0^\infty p(\rho)d\rho + \int_0^\infty p(\rho)\log\frac{p(\alpha\rho)}{p(\rho)}d\rho\right\}\\ &= N\log\alpha + N\int_0^\infty p(\rho)\log\frac{p(\alpha\rho)}{p(\rho)}d\rho. \end{aligned}\tag{28}$$

Thus we have

$$\begin{aligned}\Gamma &= -T\left(\frac{\partial S}{\partial l}\right)_T\\ &= -\frac{NkT}{l_0}\left\{\frac{1}{\alpha}+\int_0^\infty \rho p(\rho)\frac{p'(\alpha\rho)}{p(\alpha\rho)}d\rho\right\},\end{aligned}$$

or

$$\Gamma = -\frac{RTd_0}{M}\left\{\frac{1}{\alpha}+\frac{1}{\alpha^2}I\right\}, \tag{29}$$

where I denotes the integral.

$$\begin{aligned}I &= \int_0^\infty \rho p(\rho/\alpha)\frac{p'(\rho)}{p(\rho)}d\rho\\ &= \int_0^{(\pi b\lambda)^{\frac{1}{2}}} \rho p\left(\frac{\rho}{\alpha}\right)\frac{p'(\rho)}{p(\rho)}d\rho + \int_{(\pi b\lambda)^{\frac{1}{2}}}^\infty \rho p\left(\frac{\rho}{\alpha}\right)\frac{p'(\rho)}{p(\rho)}d\rho,\\ &= I_1+I_2.\end{aligned}\tag{30}$$

For evaluating the first integral we use the expression for $p(\rho)$ given by (20), and for the second integral we use that given by (19), and we obtain

$$\begin{aligned}I_1 = &-\frac{8\alpha^3}{\pi^2}\exp\left(-\frac{\pi\alpha^2}{2}\right)\left\{2+5\pi-\pi^2-\frac{3\pi-5}{\alpha^2}-\frac{6}{\alpha^4}\right\}-\frac{8\alpha^3(\alpha^2-1)}{\pi^2}\phi\left(\frac{\pi-1}{2}\alpha^2\right)+\frac{32\alpha^3}{\pi^2e^{4\pi}}\exp\left(-\frac{\pi\alpha^2}{2}\right)\\ &\times\left\{\frac{(176-36\pi+18\pi^2)\alpha^2-18\pi-16}{8+\alpha^2}+\frac{(72\pi+32)\alpha^2-36}{(8+\alpha^2)^2}+\frac{144\alpha^2}{(8+\alpha^2)^3}-\frac{2(\alpha^2-1)}{\pi-1}\right\}\\ &-\frac{32\alpha^3(\alpha^4-5\alpha^2+2)}{\pi^2e^4}\phi\left\{\frac{\pi-1}{2}(8+\alpha^2)\right\}+\frac{8\alpha^3}{\pi^2}\exp\left(-\frac{9\pi\alpha^2}{2}\right)\left\{\pi^2-5\pi-2+\frac{3\pi-5}{9\alpha^2}+\frac{2}{27\alpha^4}\right\}\\ &-\frac{8(9\alpha^2-1)\alpha^3}{\pi^2\exp(4\alpha^2)}\phi\left\{\frac{9(\pi-1)}{2}\alpha^2\right\}\cdots,\end{aligned}\tag{31}$$

* In making the above assumption, we ignore those molecule-chains which in the unstretched state of rubber already possess a length comparable to λ. As almost all the chains have their length lying between 0.5 $(\lambda b)^{\frac{1}{2}}$ and 3.5 $(\lambda b)^{\frac{1}{2}}$, the maximum permissible value of α is of order $(\lambda/b)^{\frac{1}{2}}$.

$$I_2=-4\sqrt{2}\alpha^2\sum_1^\infty(-)^{k-1}\left\{\exp\left(-\frac{\pi k^2}{2\alpha^2}\right)+\frac{\alpha}{k}\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\text{Erfe}\left[\frac{k}{\alpha}\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\right]\right\}+48\sqrt{2}\alpha^2\sum_1^\infty(-)^{k-1}\frac{k^2}{3\alpha^2+k^2}$$

$$\times\left\{\exp\left[-\left(3+\frac{k^2}{\alpha^2}\right)\frac{\pi}{2}\right]+\alpha\left(\frac{2}{(3\alpha^2+k^2)\pi}\right)^{\frac{1}{2}}\text{Erfe}\left[\frac{1}{\alpha}\left(\frac{\pi(3\alpha^2+k^2)}{2}\right)^{\frac{1}{2}}\right]\right\}+192\sqrt{2}\alpha^2\sum_1^\infty(-)^{k-1}$$

$$\times\frac{k^2}{6\alpha^2+k^2}\left\{\exp\left[-\left(6+\frac{k^2}{\alpha^2}\right)\frac{\pi}{2}\right]+\alpha\left(\frac{2}{(6\alpha^2+k^2)\pi}\right)^{\frac{1}{2}}\text{Erfe}\left[\frac{1}{\alpha}\left(\frac{\pi(6\alpha^2+k^2)}{2}\right)^{\frac{1}{2}}\right]\right\}, \quad (32)$$

where

$$\phi(x)=\int_x^\infty\frac{e^{-w}}{w}dw,$$

and

$$\text{Erfe}\,(x)=\int_x^\infty\exp(-w^2)dw.$$

In the case of $\alpha\sim1$ we have directly from (29)

$$\Gamma=12.6\frac{RTd_0}{M}\frac{l-l_0}{l_0}, \quad (33)$$

and for $\alpha\gg1$

$$\Gamma\sim4\log 2\frac{RTd_0}{M}\frac{l}{l_0}. \quad (34)$$

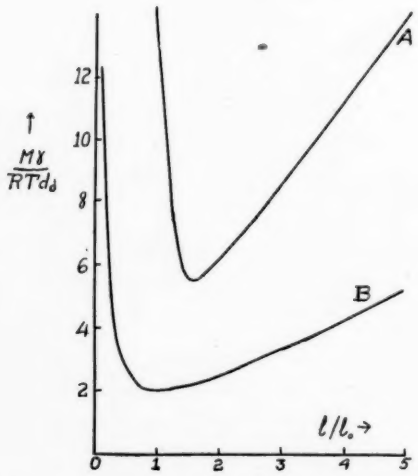

FIG. 1. The curves in the figure show the relation between Young's modulus γ and the stretched length l. The curve A is based on *chain-length*, and the curve B on *ends-separation* of the chain.

Thus we have for the isothermal Young's modulus

$$\gamma=l\left(\frac{\partial\Gamma}{\partial l}\right)_T=\alpha\left(\frac{\partial\Gamma}{\partial\alpha}\right)_T$$

$$=\begin{cases}12.6\dfrac{RTd_0}{M} & \text{for } \alpha\sim1\\ 4\log 2\dfrac{RTd_0}{M}\dfrac{l}{l_0} & \text{for } \alpha\gg1.\end{cases} \quad (35)$$

When $\alpha\ll1$, i.e., for the case of high compression, Eq. (29) gives

$$\gamma=\frac{3\pi^2RTd_0}{2M}\frac{l_0^3}{l^3}. \quad (36)$$

The curve A in Fig. 1 exhibits the relation between γ and l/l_0 as determined from Eqs. (29), (31), and (32). The curve B represents the same relation as given by Eq. (17) which is derived on the basis of ends-separation of a molecule-chain. The extension to three dimensions and the comparison of the theoretical results with experiment will be taken elsewhere. The purpose of the present paper is to show how the results of the usual theory are modified when the *chain-length* and not the *distance between the ends* of the chain is taken as the parameter to define a macro-state of the molecule-chain.

Letters to the Editor

PROMPT publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is the third of the month. Because of the late closing date for the section no proof can be shown to authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not in general exceed 600 words in length.

Gel Formation in Vinyl-Divinyl Copolymers*

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THE gelation of polymerizing systems containing multifunctional reactants has been shown by Flory[1] to be due to the sudden formation of macroscopic network molecules. For polycondensations, in which the reaction mechanism is very simple, a statistical theory can be formulated which permits a rather accurate prediction[1] of the extent of reaction at which gelation occurs. In the case of vinyl polymerizations, on the other hand, a completely *a priori* prediction of the gel point is not feasible because the mechanism is complex and but imperfectly understood. Conversely, however, experimental observations of the gel point may be used to study certain features of the reaction mechanism, as we shall indicate below.

In a polymerizing mixture of monovinyl and divinyl reactants (subject to the experimentally realizable condition that all double bonds are equally reactive and hence enter the chains at random), we find that the expected number of cross-links to which a given cross-link is connected by a single chain is $p\rho(\lambda_w-1)$, where p is the fraction of reacted double bonds, ρ is the over-all fraction of double bonds residing on divinyl units, and λ_w is the *weight average* number of reacted double bonds in a stable polymer chain. As Flory[1] has shown, as soon as this expectance exceeds unity there is a finite probability that very large cross-linked molecules shall form, so that the extent of reaction at the gel point is

$$p_c=1/\rho(\lambda_w-1). \qquad (1)$$

Actually Eq. (1) gives a lower limit for p_c, since intramolecular reactions leading to cyclic structures are not allowed in the derivation, but the error is quite small.[1]

It is to be emphasized that in deriving Eq. (1) no assumptions are made concerning the reaction mechanism other than the aforementioned one that all double bonds are equally reactive. This condition can be realized by a proper choice of reactants if, as has been demonstrated for polyesterifications[2] and is very likely in vinyl polymerizations,[3] the rates of all steps in the polymerization process are independent of the size of the molecules on which the reacting functional groups are located. This state of affairs does not, as was erroneously implied in another paper,[4] necessarily lead to the same molecular size distribution found in polycondensation reactions, which involve only a single reiterated step.

We note further that "branching" reactions (e.g., transfer of a hydrogen atom from one free radical to another, resulting in a stable molecule and a biradical) are not excluded from the mechanism, so that the "chains" whose weight average length λ_w enters Eq. (1) are not necessarily linear. They may be pictured as the aggregates that would remain if all the divinyl units were suddenly to be chopped in half.

Since p_c and ρ are easily measured, Eq. (1) appears to offer a new and very simple method of studying the variation of λ_w with temperature, concentrations, and extent of reaction. It has special interest for systems in which the rates are independent of ρ, for in such cases λ_w is identical with the weight average degree of polymerization of the pure monovinyl system. One might presume such a condition to exist if the divinyl units are essentially dimers of the monovinyl units (for example, vinyl acetate and divinyl succinate, methyl methacrylate and glycol dimethacrylate, etc.), since the effects of changing medium would then be at a minimum. Alternative ways of measuring λ_w are either tedious (fractionation, sedimentation) or of unknown validity (viscosity).

Equation (1) also applies, with a redefinition of symbols, to experiments in which previously prepared linear polymers are cross-linked by an added reagent (e.g., the vulcanization of rubber). In this case ρ signifies the fraction of units (in the polymer characterized by λ_w) susceptible to the cross-linking reaction, and p_c is the fraction (at the gel point) of such units involved in cross-links. If the chains are long and of uniform length, Eq. (1) reduces to a result previously given by Flory.[5]

We intend at a later time to present a more complete treatment of the theory, and to report on experiments now in progress.

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